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**THERMO-ELECTRICITY AND REFRIGERATION  
AT LOW TEMPERATURES**

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**Stevens Institute of Technology**

**Prepared for:**

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**31 December 1972**

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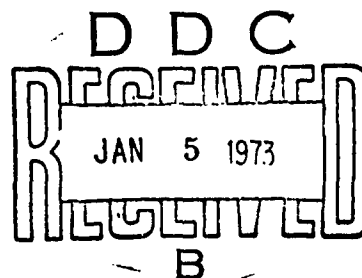
ANNUAL REPORT

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31 December 1972



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**ANNUAL REPORT**

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STEVENS INSTITUTE OF TECHNOLOGY  
HOBOKEN, NEW JERSEY**

**TO:**

Department of the Navy  
Office of Naval Research  
Washington, D. C.

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**ON:**

Thermo-electricity and Refrigeration  
at Low Temperatures

**COVERING PERIOD:**

1 January 1972 - December 31, 1972

**SUBMITTED BY:**

  
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Dr. John G. Daunt  
Director, Cryogenics Center

**DATE:**

December 31, 1972

# THERMOELECTRICITY AND REFRIGERATION AT LOW TEMPERATURES

## 1. Personnel

The following persons have been associated with the project during the period covered by this report.

Dr. John G. Daunt	Director, Cryogenics Center
Dr. E. Lerner	Assistant Professor
Dr. G. J. Goellner	Research Associate
Dr. D. C. Hickernell	Research Associate
Dr. D. L. Husa	Research Associate
Dr. R. J. Roberts	Research Associate
Mr. S. G. Hegde	Research Assistant
Mr. P. Mahadev	Research Assistant
Mr. S. N. Mahajan	Research Assistant
Mr. J. Sangeorge	Research Aide
Mr. E. Karan	Research Aide
Mr. W.H.P. Van Iperen	Research Aide
Miss O. Mezzina	Secretary

## 2. Research Program

The research programs are:

- (1) Thermoelectricity at very low temperatures.
- (2) Physics of Adsorbed Gas Layers and Desorption Refrigeration.
- (3) Experimental Studies of Cryogenic Refrigeration.

Under (1) The absolute thermo-electric power  $S$ , of long single crystals of 99.9999% pure gallium have been measured as a function of temperature, crystal orientation, size and impurities between 4.2K and 1.4K using a superconducting quantum interference galvanometer with sensitivity of  $10^{-12}$  volts.

It was found that the anisotropy of the metal affects the thermo-power in a dramatic way. The algebraic sign of the thermo-electric power along the A and B axes was positive throughout the temperature range covered and for all the sizes employed. The thermo-electric power along the C-axis changed sign from positive to negative as the temperature was reduced. All the results in-

indicated that the thermo-electric power,  $S(i)$ ,  $i=A, B$  or  $C$ , was a monotonically increasing function of temperature and for constant size  $S(A) > S(B) > S(C)$ . Furthermore  $S$  increased as the diameter ( $d$ ) of the sample was reduced. The values of the measured  $S$  ranged between  $-2.0$  to  $12.0 \times 10^{-8}$  V/°K.

The temperature dependence of  $S$  along the A and B-axes is explained on the basis of contributions from (1) electron diffusion, (2) phonon drag, (3) processes which contribute to deviations from Matthiessen's rule in the electrical resistivity and (4) higher order electron-phonon processes (so-called "phoney phonon drag"). The temperature dependence of  $S$  along the C-axis is interpreted on the basis of an approach suggested by Bailyn (1960), which was applied to data on the alkali metals by MacDonald et. al. (1960), assuming the existence of Umklapp electron-phonon scattering.

The variation of the diffusion thermo-electric power with changes in the dimensions of the samples is obtained by extrapolation of the data to absolute zero. The size-dependent behavior is then discussed in terms of a simple model based on Nordheim's rule (1935) and the sign and the order of magnitude of the rate of change with energy of the electronic mean free path  $(\partial \ln \ell / \partial E)$  and of the Fermi-surface area  $(\partial \ln A / \partial E)$  is obtained and compared with the results obtained on gold by Huebner (1964). The value of  $(\partial \ln A / \partial E)$  is negative for all three axes and its magnitude is smallest for B-axis and largest for C-axis. The quantity  $(\partial \ln \ell / \partial E)$  is positive for all three axes.

In addition, the thermo-electric power of gallium alloys with the indium and tin as impurity was also measured. The results are interpreted in the light of recent theoretical predictions of Nielsen and Taylor (1970). The characteristic thermo-electric power of indium and tin as a function of temperature is obtained using Kohler's (1949) formula.

Two papers on the above work are being prepared for publication.

Under (2) a great deal of work has been done and this is reported in the following papers, reprints of which are included in this Report:

1. "Absorption of  $\text{He}^3$  and  $\text{He}^4$  on various substrates below 30K". J.G. Hegde and E. Lerner, Proc. 2nd Internat. Symp. on "Adsorption & Desorption Phenomena", Florence, Apr. 1971. p. 127. Published by Academic Press, 1972.
2. "Measurement of Molecule-Surface Binding Energies by a Time-of-Flight Diffusion Method", F. Pollock, H. Logan, J. Hobgood and J.G. Daunt. Phys. Rev. Letters 28, 346, 1972.
3. "Adsorption of  $^3\text{He}$  and  $^4\text{He}$  on Copper and on Argon-coated Copper below 20K", J.G. Daunt and E. Lerner, Journal Low-Temperature. Phys. 8, 79. 1972
4. "Transitions in Neon Submonolayers Adsorbed on Argon Coated Grafoil", E. Lerner, S.G. Hegde and J.G. Daunt. Phys-Letters. 41A, 239. 1972.
5. "The Specific Heats of Submonolayers of  $^4\text{He}$  Adsorbed on Copper and on Argon and Neon monolayers on Copper at Low Temperatures". P. Mahadev, M. F. Panczyk, R. A. Scribner and J. G. Daunt. Phys. Letters 41A. 221. 1972.
6. "Some Properties of Two Phase Submonolayers of Adsorbed Helium". J. G. Daunt. Phys. Letters. 41A, 223. 1972

7. "Desorption Cooling below 12K using He<sup>4</sup> desorbed from Synthetic Zeolite", J. G. Daunt and C. Z. Rosen. Cryogenics 12, 201. 1972

Under (3) we have designed, constructed and put into operation a new type of refrigerator, which maintains temperatures down to 0.25K, and which only uses a supply of liquid nitrogen. Details of this refrigerator will be presented in our next Report.

*John G. Daunt*

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John G. Daunt  
December 31, 1972

## **"ADSORPTION — DESORPTION PHENOMENA"**

**Publ. Academic Press, 1972**

### **ADSORPTION OF $^3\text{He}$ AND $^4\text{He}$ ON VARIOUS SUBSTRATES BELOW $30^\circ\text{K}^*$**

**J. G. DAUNT and E. LERNER**

*Stevens Institute of Technology, Hoboken, New Jersey, USA*

#### **I. INTRODUCTION**

This paper gives a brief preliminary report on some recent measurements of adsorption isotherms of  $^3\text{He}$ ,  $^4\text{He}$  and neon deposited on copper and on argon-coated copper. It also presents some previous (Daunt and Rosen, 1970a) data on the adsorption of  $^3\text{He}$  and  $^4\text{He}$  on synthetic zeolite for comparison with the recent data. From the data the isosteric heats of adsorption are calculated as a function of coverage, and information regarding the monolayer coverage is deduced.

#### **II. THE EXPERIMENTAL ARRANGEMENTS**

The measurements were made using apparatus which has been described elsewhere (Daunt and Rosen, 1970a). The range of pressures covered was from about 0.25 mmHg to 75 mmHg and the temperature range from  $4.2^\circ\text{K}$  to  $26^\circ\text{K}$ . The filling tube going from room temperature down to the cold specimen chamber had an inner diameter 2.16 mm. The thermomolecular pressure corrections necessitated by this tube, which connected the specimen at the low temperature to the pressure gauge at room temperature, were not greater than 3% for pressures of 0.5 mmHg and above. All necessary corrections for void volumes, gas non-ideality, etc. were carried out in the same manner as described previously (Daunt and Rosen, 1970a).

The copper surface for these adsorption studies was made in the form of a sponge by sintering pressed copper powder ("Druid Copper", Grade MD60 made by Alcan Metal Powders Inc.) of average particle size  $2 \times 2 \times 0.5$  microns in a hydrogen furnace at  $650^\circ\text{C}$  for 0.5 hours. This construction assured temperature

\* Work supported by a contract with the Department of Defense (Themis Program), the Office of Naval Research and by a Grant from the National Science Foundation.



homogeneity over the whole adsorbing surface. The specimen used in the measurements comprised three such copper sponges in the form of discs, 5.00 cm dia. and 0.68 cm thick each, with a total mass of 170 g. The filling factor was 47.7%.

### III. THE SURFACE AREA OF THE COPPER SPONGE

The surface area,  $\Sigma$ , of the specimen was obtained from measurements of adsorption isotherms of  $N_2$  and argon taken at 77.3°K. The isotherms proved very reproducible and showed no hysteresis. They were typical Type II isotherms (Young and Crowell, 1962) and the value of the monolayer coverage,  $V_m$ , was estimated by the "Point B" method (Young and Crowell, 1962). The results are given in table 1.

Table 1. The monolayer coverage,  $V_m$ , and the surface area  $\Sigma$  as deduced from  $N_2$  and argon isotherms on a copper sponge at 77.3°K (see text). The molecular areas,  $\sigma$ , are taken from Young and Crowell (1962)

Substance	$V_m$ cm <sup>3</sup> (STP)/g	$\sigma$ Å <sup>2</sup>	$\Sigma$ m <sup>2</sup> /g
$N_2$	0.11	16.2 (liquid)	0.48
$N_2$	0.11	13.8 (solid)	0.41
Ar	0.11	13.8 (liquid)	0.41
Ar	0.11	12.8 (solid)	0.38

The surface area  $\Sigma$  in m<sup>2</sup>/g was calculated from  $V_m$ , using the formula (Young and Crowell, 1962)

$$\Sigma = 0.269 V_m \sigma$$

where  $\sigma$  is the molecular area of the adsorbed gas in Å<sup>2</sup> and  $V_m$  is in cm<sup>3</sup>(STP)/g. As has been discussed many times, and reviewed, for example in a previous paper (J. G. Daunt and C. Z. Rosen, 1970a), there is a question as to whether the  $\sigma$  for  $N_2$  should be taken to be that for the liquid state (16.2 Å<sup>2</sup>) or that for the solid state (13.8 Å<sup>2</sup>). In table 1 we show the values of  $V_m$  and  $\Sigma$  for  $N_2$  and Argon obtained from our 77.3°K isotherms, where  $\Sigma$  is deduced from  $\sigma$  values both for the liquid and the solid state. It will be seen that  $\Sigma$  deduced from the  $N_2$  (solid) isotherm is about 8% lower than that obtained from the argon (solid) isotherm. A similar discrepancy between the  $N_2$  and argon data for evaluation of  $\Sigma$  was observed previously (Daunt and Rosen, 1970a) in our synthetic zeolite adsorption measurements. The cause of the discrepancy is not

clear, but may be associated with some uncertainty in the value of  $\sigma$  for argon.

We have chosen  $\sigma$  for solid  $\text{N}_2$  as appropriate for calculation of  $\Sigma$ , giving a result of  $\Sigma = 0.41 \text{ m}^2/\text{g}$  for our copper sponge. This value has been used in all data presented in this paper.

#### IV. THE MEASURED ISOTHERMS

Figures 1 and 2 show the adsorption isotherms of  $^4\text{He}$  on the clean bare copper sponge and on a monolayer of argon deposited on the same sponge at the following temperatures:  $6.18^\circ\text{K}$ ,  $7.90^\circ\text{K}$ ,  $9.65^\circ\text{K}$ ,  $11.60^\circ\text{K}$ ,  $13.50^\circ\text{K}$ ,  $15.08^\circ\text{K}$

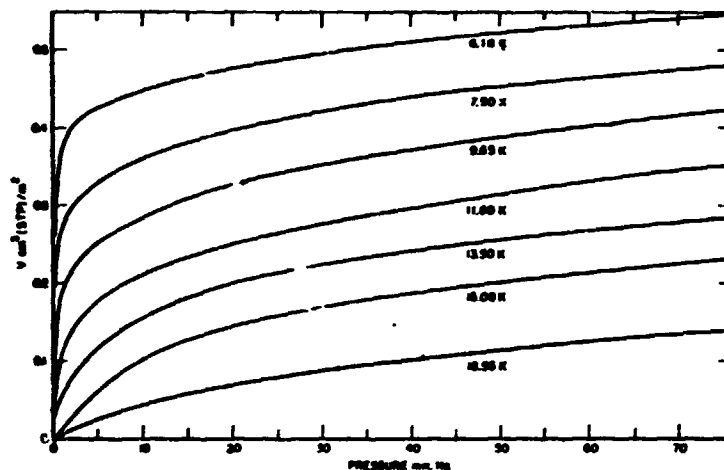


Fig. 1. Adsorption isotherms for  $^4\text{He}$  on bare Cu at temperatures as marked.

and  $18.55^\circ\text{K}$ . In depositing the argon, an amount of argon gas corresponding to the measured amount required at  $77.3^\circ\text{K}$  to form a monolayer was admitted to the sample cell at room temperature, the cell was then cooled slowly over a period of 19 hours from room temperature to liquid helium temperature. This permitted adequate time for the argon to diffuse throughout the copper sponge and to deposit evenly on it. By comparing figures 1 and 2, it will be noted that at any given temperature and pressure, the amount of  $^4\text{He}$  adsorbed on the argon covered copper sponge is less than that adsorbed on the bare sponge.

The data for  $^3\text{He}$  adsorbed on bare copper at the same selected temperatures are shown in figure 3. By comparison with figure 1 for  $^4\text{He}$  on bare copper, it will be seen that the  $^3\text{He}$  curves show smaller adsorption at any given temperature and pressure. However at the highest temperatures and pressures reported these differences are very small and within experimental error. This

result is in qualitative agreement with the comparison of adsorption of  $^3\text{He}$  and  $^4\text{He}$  on synthetic zeolite 13X as shown in figures 4 and 5 and as reported previously (Daunt and Rosen, 1970a).

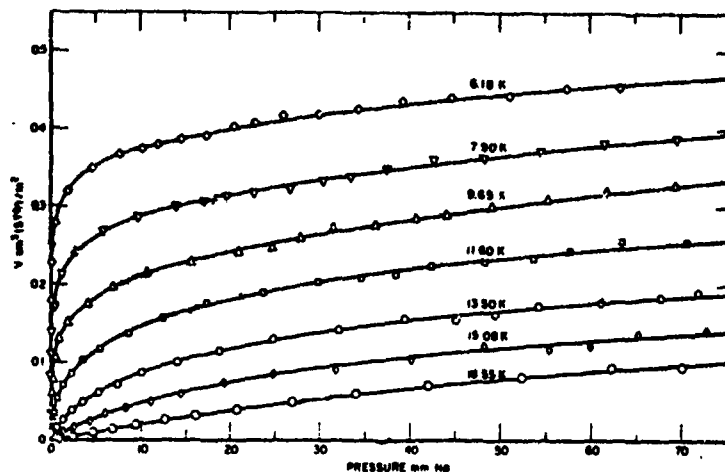


Fig. 2. Adsorption isotherms for  $^4\text{He}$  on monolayer of argon on Cu at temperatures as marked.

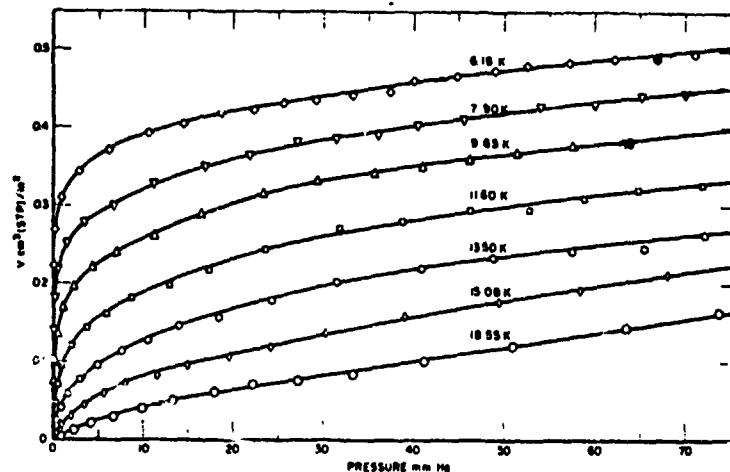


Fig. 3. Adsorption isotherms for  $^3\text{He}$  on bare Cu at temperatures as marked.

Comparison of figures 2 and 3 shows that the introduction of an argon monolayer on the copper lowers the adsorption of  $^4\text{He}$ , even below that of  $^3\text{He}$  on bare copper.

In order to make a qualitative and quantitative comparison of the results using the copper sponge with earlier ones using synthetic zeolite, we show in

figures 4 and 5, on the same scale in  $\text{cm}^3(\text{STP})/\text{m}^2$ , the adsorption isotherms for  $^4\text{He}$  and  $^3\text{He}$  on synthetic zeolite (Linde Molecular Sieve, Type 13X) as measured in our laboratory previously (Daunt and Rosen, 1970a) at the

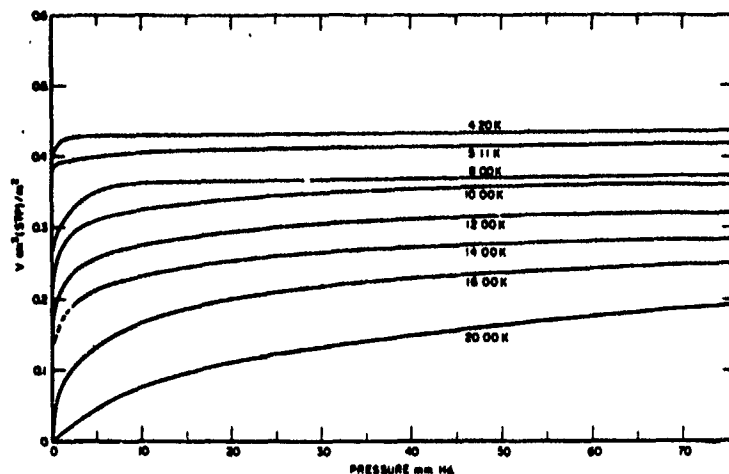


Fig. 4. Adsorption isotherms of  $^4\text{He}$  on synthetic zeolite 13X at temperatures as marked.

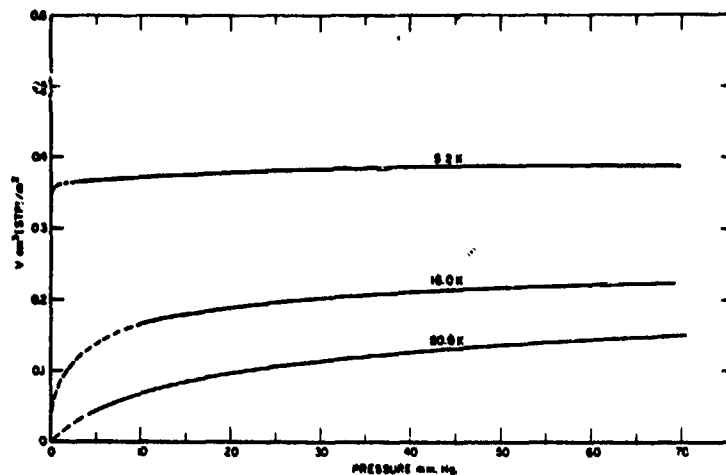


Fig. 5. Adsorption isotherms of  $^3\text{He}$  on synthetic zeolite 13X at temperatures as marked.

following temperatures:  $4.2^\circ\text{K}$ ,  $5.11^\circ\text{K}$ ,  $8.0^\circ\text{K}$ ,  $10.0^\circ\text{K}$ ,  $12.0^\circ\text{K}$ ,  $14.0^\circ\text{K}$ ,  $16.0^\circ\text{K}$  and  $20.0^\circ\text{K}$ . The character of these adsorption curves seems to differ from those found with the copper sponge; they appear much "flatter" in the higher pressure ranges. This may be associated with much smaller sizes of the voids in the zeolite.

Figure 6 shows the measured neon adsorption isotherms on the bare copper sponge and on the copper sponge coated with a monolayer of argon at 22.6°K and at 25.75°K. Here the much lower adsorption on the argon monolayer as compared with the adsorption on the bare copper is clearly evident.

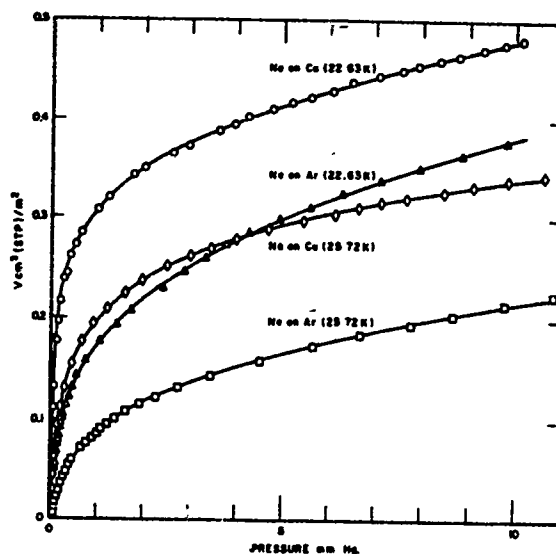


Fig. 6. Adsorption isotherms for neon on bare Cu and on monolayer of argon on Cu at temperatures as marked.

## V. THE ISOSTERIC HEAT OF ADSORPTION

The data of figures 1, 2, 3, 4, and 6 have been used to construct plots of  $\ln p$  versus  $1/T$  for various constant coverages ( $V$  constant). It was found that these plots were linear over a wide range of temperature. The slope,  $|\partial \ln p / \partial (1/T)|V$ , is equal to  $Q_{st}/R$ , where  $Q_{st}$  is the isosteric heat of adsorption. The results of these computations are shown in figures 7 and 8 which give  $Q_{st}/R$  in degrees Kelvin as a function of the coverage,  $V$  in  $\text{cm}^3(\text{STP})/\text{m}^2$ .

Figure 7 shows the results for neon on bare copper and on copper covered with a monolayer of argon; for  $^4\text{He}$  on the bare copper and, for comparison, for  $^4\text{He}$  on synthetic zeolite (Linde Molecular Sieve, 13X). The latter results were recomputed from data presented in a previous paper (Daunt and Rosen, 1970a).

It will be seen that  $Q_{st}$  is significantly lower at all coverages for neon on a monolayer of argon deposited on copper than for neon on bare copper. At a

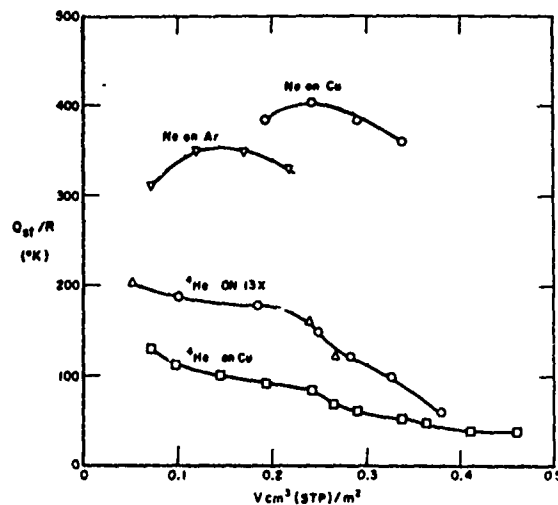


Fig. 7. The isosteric heat of adsorption,  $Q_{st}/R$ , as a function of coverage  $V/\Sigma$  for: Neon on bare Cu and on monolayer of argon on Cu;  $^4\text{He}$  on synthetic zeolite 13X and  $^4\text{He}$  on bare Cu.

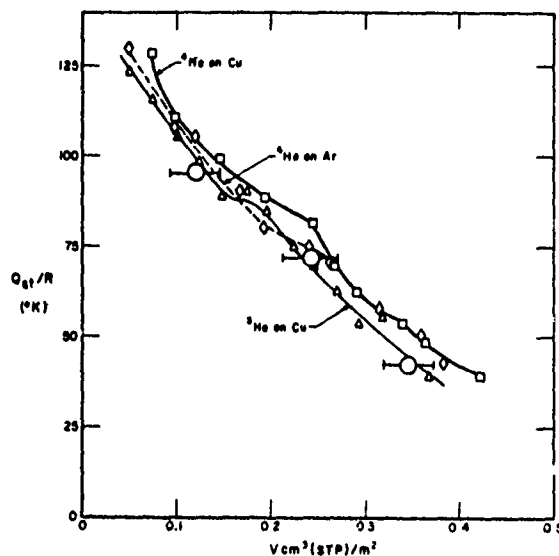


Fig. 8. The isosteric heat of adsorption,  $Q_{st}/R$ , as a function of coverage  $V/\Sigma$  for  $^4\text{He}$  on bare Cu and on monolayer of argon on Cu; —○— (Wallace and Goodstein, 1970) and  $^3\text{He}$  on bare Cu.

coverage of  $0.24 \text{ cm}^3(\text{STP})/\text{m}^2$ ,  $Q_{st}/R$  for neon on copper is  $400^\circ\text{K}$  and for neon on a monolayer of argon on copper  $Q_{st}/R$  is  $320^\circ\text{K}$ .

Figure 7 shows that the  $Q_{st}$  values for  $^4\text{He}$  are significantly lower than those for neon. At a coverage of  $0.24 \text{ cm}^3(\text{STP})/\text{m}^2$   $Q_{st}/R$  is  $83^\circ\text{K}$  for  $^4\text{He}$  on bare copper and  $162^\circ\text{K}$  on synthetic zeolite 13X. As is clearly shown in figure 7,  $Q_{st}$  for  $^4\text{He}$  on bare copper is much lower than that on zeolite 13X at any chosen coverage below about  $0.4 \text{ cm}^3(\text{STP})/\text{m}^2$ . The  $Q_{st}$  values for neon are not as secure as those for  $^4\text{He}$ , because of the relatively much smaller number of isotherms of neon from which calculations are made. This relative imprecision particularly refers to the coverage dependence of  $Q_{st}$ .

Figure 8 shows  $Q_{st}/R$  versus coverage for  $^3\text{He}$  and  $^4\text{He}$  on the bare copper and for  $^4\text{He}$  on a monolayer of argon on copper. It also shows three points taken from extensive data by Wallace and Goodstein (1970) for  $^4\text{He}$  on a monolayer of argon on copper. The agreement between our results and those of Wallace and Goodstein is fair and probably within the errors introduced in the normalization of Wallace and Goodstein's data to our own.\*

It appears that  $Q_{st}$  at any chosen coverage for  $^4\text{He}$  on the bare copper is higher than that for  $^3\text{He}$  also on the bare copper. In comparing  $^4\text{He}$  on bare copper and on the argon monolayer, it appears that below a coverage of about  $0.25 \text{ cm}^3(\text{STP})/\text{m}^2$ ,  $Q_{st}$  on argon is smaller than on the bare copper, however above the stated coverage there appears to be little difference between the observed  $Q_{st}$  values.

Although the precision in the  $Q_{st}$  values is much poorer than those in the observed adsorption isotherms, a feature which makes it difficult to interpret closely the variation of  $Q_{st}$  with coverage, two main features appear in figures 7 and 8 for the helium data, namely

(1) There appears to be a change in slope, or perhaps an inflexion at about  $V = 0.24$  for  $^4\text{He}$  both on bare copper and on the argon monolayer and at about  $0.17 \text{ cm}^3(\text{STP})/\text{m}^2$  for  $^3\text{He}$  on bare copper.

(2) Both above and below these coverages,  $Q_{st}$  is dependent on coverage and shows little sign of becoming independent of coverage even at the coverages observed.

We interpret these two features as follows:

(1) The inflexions are interpreted as indicating the approximate coverage at which the first layer of adsorbed gas is completed. This yields  $V_m$  values as follows: For  $^4\text{He}$  on bare copper and on the argon monolayer on copper  $V_m \approx 0.24 \text{ cm}^3(\text{STP})/\text{m}^2$ . For  $^3\text{He}$  on bare copper  $0.17 \text{ cm}^3(\text{STP})/\text{m}^2$ . These

\* To normalize Wallace and Goodstein's (1970) data to our own, we have taken our  $^4\text{He}$  on the argon monolayer to have a monolayer capacity,  $V_m$ , of  $0.24 \text{ cm}^3(\text{STP})/\text{m}^2$  as explained in the text above. No change has been made in Wallace and Goodstein's data, nor can a comparison of our  $V_m$  value with their data be made, since they did not specify the surface area of their adsorbent

values are to be compared with some previous values, such those of McCormick *et al.* (1968) who quoted  $V_m \approx 0.33$  for  $^4\text{He}$  and 0.29 for  $^3\text{He}$  on bare copper and those of Daunt and Rosen (1970a) who quoted  $V_m$  to be probably less than  $0.29 \text{ cm}^3(\text{STP})/\text{m}^2$  for  $^4\text{He}$  on synthetic zeolite and  $0.26 \text{ cm}^3(\text{STP})/\text{m}^2$  for  $^3\text{He}$  on the same adsorbent (Daunt and Rosen, 1970b).

Table 2. Data of isosteric heat ( $Q_{st}$ ) and estimated monolayer coverage ( $V_m$ ).

	$Q_{st}/R$ (K) At monolayer capacity	$V_m$ $\text{cm}^3(\text{STP})/\text{m}^2$
$\text{He}^3$ on bare copper	88	0.17
$\text{He}^4$ on bare copper	83	0.24
$\text{He}^4$ on Ar monolayer on Cu	76	0.24

	$Q_{st}/R$ (K) At $V = 0.24 \text{ cm}^3(\text{STP})/\text{m}^2$
Neon on bare copper	400
Neon on Ar monolayer on Cu	320

The observation that  $V_m$  for  $^4\text{He}$  appears to be approximately the same for adsorption on bare copper as on the argon monolayer, taken with the fact that the  $Q_{st}$  values do not differ significantly for the two substrates, presumably indicates that the surface area for adsorption is not different for the two substrates.

(2) The way  $Q_{st}$  continues to increase as the coverage is reduced below the monolayer coverage for the helium on all substrates used is interpreted as indicating inhomogeneity of adsorbing sites.

We sum up our data on  $Q_{st}$  and  $V_m$  values in table 2, which gives our evaluation of the quantities on the various substrates at monolayer coverage.

#### REFERENCES

- Daunt, J. G. and Rosen, C. Z. (1970a). *J. Low Temp. Phys.* 3, 89  
 Daunt, J. G. and Rosen, C. Z. (1970b). *Proc. Symp. Thermo. Phys. Prop.* 5th, p. 319.  
 McCormick *et al.* (1968). *Phys. Rev.* 168, 249.  
 Wallace, J. L. and Goodstein, D. L. (1970). *J. Low Temp. Phys.* 3, 283.  
 Young, D. M. and Crowell, A. D. (1962). In "Physical Adsorption of Gases". Butterworth, London.



# Measurement of Molecule-Surface Binding Energies by a Time-of-Flight Diffusion Method\*

F. Pollock, H. Logan,<sup>†</sup> J. Hobgood,<sup>‡</sup> and J. G. Daunt

*Physics Department and Cryogenics Center, Stevens Institute of Technology, Hoboken, New Jersey 07030*

(Received 5 November 1971)

A kinetic method for measuring the properties of solid surfaces is described, and results are reported for the binding of helium on copper and copper thickly plated with argon.

The purpose of this paper is to describe a technique for studying the properties of solid surfaces and to report the results of the initial investigations on atomic binding energy to surface sites using this method. The method uses kinetic rather than static measurements. In the first series of experiments we have measured characteristic times for the transit of a pulse of helium gas through a long narrow tube (tube diameter  $<$  mean free path for molecule-molecule collision). Keeping in mind that the arguments apply to other geometries, we shall use this one to fix our ideas. Provided the gas of the input pulse is sufficiently dilute, the molecules execute a one-dimensional random walk with each step terminating at the tube wall. The rate of transit down a tube depends on the diffusion constant for one-dimensional motion which is given by

$$D = \frac{1}{2} \bar{X}^2 / \bar{\tau}, \quad (1)$$

where  $\bar{X}^2 \sim (\text{diameter})^2$  is the mean square step length and is essentially temperature independent, and  $\bar{\tau}$  is the mean step time which does depend on the temperature of the system. There are two contributions to  $\bar{\tau}$ . First, there is the kinetic part  $\bar{\tau}_f$ , depending on the temperature through the rms molecular speed. This part should vary as  $T^{-1/2}$ . For our geometry  $\bar{\tau}_f \sim 10^{-5} - 10^{-6}$  sec. The other, more interesting part, is the capture time on the surface. One expects that its principal temperature dependence will be exponential, and arguments can be made making this conjecture more precise. If, now,  $\xi$  is the probability that an incident particle will be captured and  $\bar{\tau}_c$  the capture time, one can write for  $\bar{\tau}$

$$\bar{\tau} = (1 - \xi) \bar{\tau}_f + \xi (\bar{\tau}_f + \bar{\tau}_c) = \bar{\tau}_f + \xi \bar{\tau}_c. \quad (2)$$

Thus, any characteristic time of the diffusion process will depend on  $\bar{\tau}_f$  and the product  $\xi \bar{\tau}_c$ .

An analysis of the adsorption-desorption process can be made analogous to the Einstein treatment of the adsorption and emission of radiation by atoms. Here, since the processes depend on surface and molecular properties and the temperature of the system, we may consider a system

in equilibrium at temperature  $T$ , consisting of a gas of  $N_0$  molecules of interest in a volume  $V$ , surrounded by a surface made of the solid of interest whose area is  $A$ . We assume a single binding energy per site of  $W$  ( $W > 0$ ) and  $\nu$  sites per unit area. The density of atoms both in the gas and on the surface is low so that molecule-molecule interactions may be safely neglected.

We then have a simple problem in statistical mechanics. The density of particles on the surface is

$$\sigma = Z^{-1} N_0 \exp(W/kT), \quad (3)$$

where  $Z$  is the single-particle partition function. The gas density is

$$\rho = \frac{N_0}{Z} \frac{1}{(2\pi\hbar)^3} \int \exp\left(\frac{-p^2}{2mkT}\right) d^3p \quad (4)$$

From elementary kinetic theory, the flux of molecules striking the surface is

$$j = \frac{1}{4} \rho \bar{v}, \quad (5)$$

where  $\bar{v}$  is the rms molecular speed, and the number captured per unit time per unit area is, by definition of the capture probability  $\xi$ ,

$$d\sigma/dt_{\text{adsorption}} = \frac{1}{4} \xi \rho \bar{v}. \quad (6)$$

From the definition of the mean lifetime  $\tau_c$  we have

$$d\sigma/dt_{\text{desorption}} = -\sigma/\tau_c. \quad (7)$$

Detailed balance then gives

$$\xi \bar{\tau}_c = \frac{4\sigma}{\rho \bar{v}} = \frac{(2\pi\hbar)^3}{2\pi m} \frac{\nu}{k^2 T^2} e^{W/kT}, \quad (8)$$

which is the result we sought and which has the interesting property that while  $\xi$  and  $\bar{\tau}_c$  separately depend, sensitively perhaps, on dynamical details of the molecule-surface interaction, their product depends only on gross properties—the binding energy, the density of sites, and the molecular mass.<sup>1</sup>

The pre-exponential factor in (8) is very small compared with  $\bar{\tau}_f$  for all interesting temperatures. The consequence of this is that one must

operate at temperatures much lower than  $W/k$  to detect the effect of capture time. As a result the time of transit of the pulse is extremely sensitive to both the temperature and the binding energy. Typically, binding energies between 100 and 200°K require operating at temperatures between 5 and 11°K. With the use of noble gases we have then a very sensitive yet gentle probe of surface properties, especially since mass spectrometry makes possible the detection of a very low density of molecules.<sup>2</sup>

The experimental arrangement is simple. In our initial experiments the transit tube was of copper, 400 cm long and 0.32 cm i.d., which could be maintained isothermally at any temperature in the range 4.2 to 77°K. Helium gas could



FIG. 1. The output response signal from the gas detector.  $S$  is the signal strength,  $t$  is the time.

be injected into one end of the tube, at a temperature equal to that of the tube. For a measurement, a square step pulse of helium of approximately 10 cm width is introduced into one end of the evacuated tube and the time noted. The number of particles in the pulse is sufficiently small as to justify the neglect of molecule-molecule interactions both in the gas and on the surface. A mass spectrometer, in this case a standard leak detector, measures the flow of helium from the other end of the tube and the signal is displayed on a chart recorder. Typical transit times, measured to the half-height of the leading edge of the pulse, range from about 9 sec at 15°K to about 10 min or more at the low-temperature end of the range. Figure 1 shows a typical output signal. The output pulse shape is found to agree quite well with the results of one-dimensional diffusion theory with small discrepancies that are temperature dependent, i.e., at high temperatures it is slightly narrower than theory predicts, while it is wider at low temperature. This effect is not yet completely understood, but does not seem to affect the shape of the leading edge of the output pulse from which the data are taken.

The most convenient quantity to measure seems to be the time of arrival of the half-maximum on the rising slope of the output curve. From the previous considerations we can write

$$t_{1/2} = a/\sqrt{T} + (\beta/T^2)e^{W/kT}, \quad (9)$$

where a small constant term due to lead-in and lead-out delays is neglected. In Fig. 2 we show a typical curve for half times,  $t_{1/2}$ , on the bare copper surface of the transit tube (which presumably has an oxide coating and perhaps other impurities). In Fig. 3 we plot for two cases, He on bare copper and He on argon-plated copper,  $T^2(t_{1/2} - a/\sqrt{T})$  vs  $1/T$ , from the slope of which we can infer the binding energy values. For the

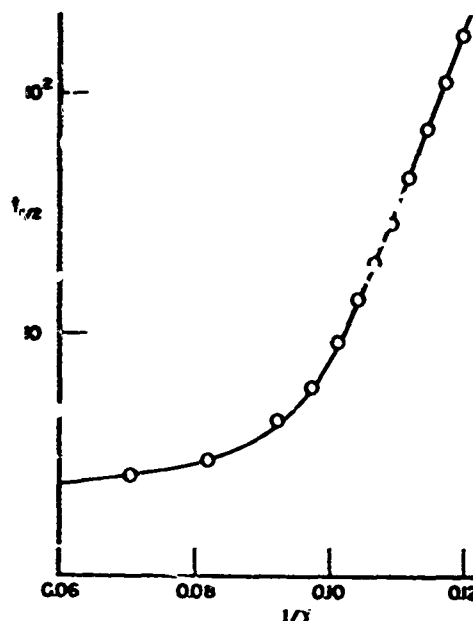


FIG. 2. The time of arrival of the half-maximum,  $t_{1/2}$ , as a function of the reciprocal of the absolute temperature. A unit of time here is 3.75 sec.

second case the tube was coated with approximately twenty layers of argon. The binding energies so obtained are  $W_{\text{He,Cu}} = 177^\circ\text{K}$  and  $W_{\text{He,Ar}} = 102^\circ\text{K}$ .

Repeated measurements on the two substrates give values that vary by roughly 5%, most of which variation is probably due to incomplete reproducibility of the temperature of the tube from run to run. We have been able to hold the temperature of the transit tube, as measured by a gas-bulb thermometer, constant usually to within less than one part per thousand. Time measurements at the low temperature are generally accurate to within 2%, while at the highest temperatures the error is probably less than 10%. This latter error is important in determining the coefficient in the  $T^{1/2}$  term, but unimportant for low tempera-

tures which are the data used for the energy determination.

It is difficult to find experimental results with which to compare our findings. Ordinary thermodynamic measurements require significant coverages, because of absolute or relative signal problems. An extrapolation to zero coverage of the results of Daunt and Lerner<sup>3</sup> for the isosteric heat of adsorption of helium on copper is roughly consistent with our results.<sup>4</sup> For the argon coating Novaco and Milford<sup>5</sup> have calculated an expected binding energy for helium on the 100 face of argon and find 100°K in very good agreement with our result of 102°K. It should be pointed out

that in our derivation of Eq. (8) we assumed only one binding state. The extension to the more general case is straightforward. In particular, except for very closely spaced levels only the most tightly bound state contributes significantly to the average sticking time. In the case of argon plating, presumably a collection of crystallites exposing some fraction of each of the crystal faces would be formed. We should expect then to see the binding on the face that binds most strongly, which from theoretical considerations is the (100) face.

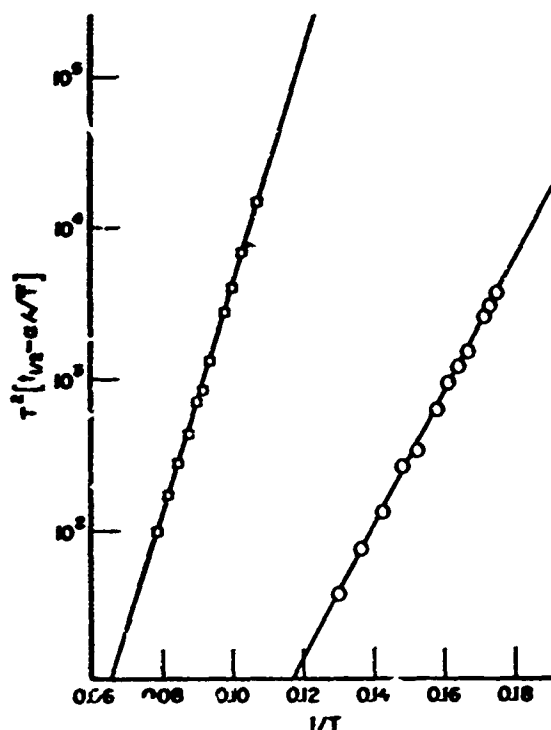


FIG. 3.  $T^2[t_{1/2} - \alpha/\sqrt{T}]$  versus the reciprocal of the absolute temperature. The squares represent the data for He on bare copper, the circles those for He on argon-plated copper.

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<sup>1</sup>Throughout this discussion it has been assumed that the diffusive process is so slow that the system is locally in equilibrium.

<sup>2</sup>It has been pointed out that quite a long time ago similar experiments were attempted. The earlier attempts were limited chiefly by detection techniques and small amounts of input gas could not be used. See J. de Boer, *The Dynamical Character of Adsorption* (Oxford Univ. Press, Oxford, England, 1968), 2nd ed.

<sup>3</sup>J. G. Daunt and E. Lerner, in *Proceedings of the Second International Symposium on Adsorption-Desorption Phenomena, Florence, Italy, 1971* (Academic, New York, 1971).

<sup>4</sup>Measurements by D. W. Princehouse (to be published) are in rough agreement with our for bare copper (private communication from Dr. J. G. Dash).

<sup>5</sup>A. D. Novaco and F. Milford, *J. Low Temp. Phys.* **3**, 307 (1970).

## Adsorption of $^3\text{He}$ and $^4\text{He}$ on Copper and on Argon-Coated Copper Below 20 K\*

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Measurements have been made of adsorption isotherms of  $^3\text{He}$  and of  $^4\text{He}$  on copper and on a monolayer of argon deposited on copper in the temperature range 6.18–18.55 K and in the pressure range 0.25 to 75 Torr. From these many isotherms, calculations have been made of the isosteric heat of adsorption  $Q_{st}/R$ . In the limit of zero coverage on the argon monolayer  $Q_{st}/R = 76 \pm 2$  K for  $^3\text{He}$  and  $76 \pm 2$  K for  $^4\text{He}$ . For adsorption on the bare copper,  $Q_{st}/R$  is difficult to extrapolate to zero coverage, but it probably lies (for both  $^3\text{He}$  and  $^4\text{He}$ ) between 135 and 165 K. At theoretical monolayer helium coverage,  $Q_{st}/R = 44 \pm 2$  K for  $^3\text{He}$  on the argon monolayer and  $47 \pm 2$  K for  $^4\text{He}$ . At theoretical monolayer helium coverage on the bare copper,  $Q_{st}/R = 61 \pm 4$  K for  $^3\text{He}$  and  $77 \pm 5$  K for  $^4\text{He}$ . The results are compared with theoretical evaluations for helium adsorbed on an argon monolayer and with some previous experimental data, and the agreement is found to be fair. All the data are summarized in tables. Finally, a review is given of evaluations, including those from this work, of the monolayer capacity of  $^3\text{He}$  and  $^4\text{He}$  on the substrates studied.

### 1. INTRODUCTION

In the last several years there has been considerable interest in the properties of adsorbed monolayers and submonolayers of the helium isotopes on relatively simple substrates, particularly on monolayers of the heavier rare gases deposited on a copper base.<sup>1-12</sup> The copper base has been chosen to assure temperature homogeneity in situations where the vapor pressure of the adsorbed helium is too small to permit heat exchange through the vapor. The selection of the helium for adsorbate and the other rare gases for adsorbent has been largely motivated by the fact that these simple systems should permit theoretical evaluations to be made of their properties.

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Moreover, the low temperature required to make meaningful experiments with helium adsorbate adds, at least in principle, a further simplicity to the interpretation of the results.

We have, therefore, made experiments on the adsorption of  $^3\text{He}$  and  $^4\text{He}$  on copper and on an argon monolayer deposited on copper in the temperature range 6.18–18.55 K. The temperature range was chosen because even monolayers or submonolayers of helium show appreciable vapor pressures in it, and, in consequence, it is possible to obtain rather easily precise data that can be used for evaluation of the isosteric heat of adsorption  $Q_{st}/R$ .

In this paper, Section 2 discusses some of the key experimental arrangements used in the measurements. Section 3 presents the observations made to determine the surface area of the substrates. For the argon monolayer substrates, we introduce a new formula for the surface area based on the assumption that monolayers of argon on copper are a close-packed array. Section 4 gives the observations of the  $^3\text{He}$  and  $^4\text{He}$  adsorption isotherms in detail and compares our results, where possible, with previous data. Section 5 details the results of calculation of the isosteric heat of adsorption  $Q_{st}/R$  for the systems studied, and, again, where possible comparison is given with previous data (Section 5) and with theory (Section 6). All the pertinent data are summarized in tables. Finally, a discussion is given in Section 7 of the monolayer capacity of the helium on the substrates studied, as revealed by theory and experiment.

## 2. EXPERIMENTAL ARRANGEMENTS

The apparatus for these measurements of adsorption isotherms was the same as that used previously and described in detail by Daunt and Rosen.<sup>13</sup> The specimen temperature could be held constant to better than  $\pm 0.005$  K at any temperature between 4.2 and 20 K. The pressure measurements ranged between 0.25 and 75 Torr. Thermomolecular pressure corrections were less than 3% for pressures above 0.5 Torr even at the lowest temperatures, and the accuracy of pressure measurement was within 0.5%. For details of the method of temperature and pressure measurement and of the corrections used in calculation of the mass adsorbed, reference is made to previous papers.<sup>13,14</sup>

The copper surface was in the form of a sintered copper sponge, first used in similar work by Dash and coworkers.<sup>1,15</sup> We used the same type of copper powder as Dash *et al.*,<sup>1,15</sup> namely, "Druid Copper" Grade MD60 from Alcan Metal Powders, Inc., which is in the form, as reported by Dash *et al.*, of flakes of mean dimension  $3\mu$ . The powder was first cleaned by soaking in suitable solvents, dried, and then partially deoxidized by baking

in a hydrogen furnace at  $300^\circ\text{C}$  for 0.5 h. It was then subsequently pressed and sintered into disks, of dimensions 5.0 cm in diameter by 0.68 cm in thickness, in an  $\text{H}_2$  furnace at  $650^\circ\text{C}$  for 0.5 h. The specimen used consisted of three such disks, of total mass 170 g and of filling factor 47.7%, which were enclosed in a good-fit copper vessel. Subsequent to mounting the specimen in the cryostat, the final cleaning procedures and preexperimental preparations were identical to those described earlier.<sup>13</sup>

The purities of the  $^3\text{He}$  and  $^4\text{He}$  used were 99.5 and 99.995%, respectively. Both were further purified by passage over activated charcoal at 77 K prior to introduction into the cryostat. The argon used was of 99.998% purity and this was further purified by passage over activated charcoal at 195 K.

In coating the specimen with a monolayer of argon, the procedure adopted has already been described by us previously.<sup>14</sup> This procedure, which was only arrived at after extensive trial-and-error methods, ensured that the argon was indeed uniformly distributed over the surface of the specimen and resulted in completely reproducible isotherms from run to run.

### 3. THE SURFACE AREA OF THE SPECIMEN

The basic experimental data used for determination of the surface area of the specimen are the adsorption isotherms of  $\text{N}_2$  and argon measured at 77.3 K. These have been previously reported by us,<sup>14</sup> along with data for neon adsorption isotherms, and graphs of these isotherms were included in that paper. It is merely necessary here to repeat that from BET analysis of these data and from "Point B" determinations (see Young and Crowell<sup>16</sup>), it was found that the monolayer coverage  $V_m$  was  $0.11 \text{ cm}^3 \text{ (STP)/g}$  for both the  $\text{N}_2$  and the argon.

The fact that the  $V_m$  values for both  $\text{N}_2$  and argon were the same was not too surprising. For example, Dash and coworkers<sup>1</sup> have reported a similar result for their sintered copper calorimeter. They reported, for a volume of  $10 \text{ cm}^3$  of sintered copper,  $V_m = 8.4 \text{ cm}^3 \text{ (STP)}$  for both  $\text{N}_2$  and argon at 77.4 K.

There has been much difficulty in the past in assessing the surface areas  $\Sigma$  from the measured  $V_m$ 's owing to questions arising as to the appropriate values of the molecular areas  $\sigma$  to employ. Quite detailed discussions of these problems have been given by Dash and coworkers,<sup>1</sup> and by Daunt and Rosen.<sup>13</sup> These have pointed up the inadequacy of the "standard" method which as reported, for example, by Young and Crowell<sup>16</sup> uses the liquid value ( $16.2 \text{ \AA}^2$ ) for  $\text{N}_2$ . The general disagreement of determinations of  $\Sigma$  from argon isotherm data as compared with the  $\Sigma$  determinations using

the "standard"  $N_2$  method is noteworthy. It is proposed therefore to adopt another procedure here, as follows.

First, it will be assumed following, for example, the work of Steele<sup>17</sup> and of Novaco and Milford<sup>5</sup> that on a metal surface, which type of surface is found\* to show no significant periodicity to adsorbate atoms, an adsorbed monolayer of argon atoms forms a close-packed array.<sup>†</sup> It is further assumed that the nearest-neighbor distance  $a$  between argon atoms is the Lennard-Jones parameter  $\rho_0$ , as has been discussed in detail by Novaco and Milford.<sup>5</sup> This is 3.83 Å, as given by Hollis-Hallett.<sup>21</sup> This gives a maximum molecular area  $\sigma$  of 11.5 Å<sup>2</sup>, which is smaller than the generally accepted<sup>16</sup> values for both liquid and solid argon. This can be understood in view of the major influence of the argon-metal attractive forces.

Now for a close-packed array of atoms with interatomic distance  $a$  equal to  $2(\sigma/\pi)^{1/2}$ , the surface area  $\Sigma$  (in m<sup>2</sup>) for  $N_m$  atoms forming a monolayer in terms of  $\sigma$  (in Å<sup>2</sup>) is

$$\Sigma(\text{m}^2) = 1.10 \times 10^{-20} \sigma N_m \quad (1)$$

or

$$\Sigma(\text{m}^2) = 0.296 \sigma V_m \quad (2)$$

where  $V_m$  is the monolayer capacity measured in cm<sup>3</sup> (STP) of the adsorbed gas. It is to be noted that the numerical coefficient in Eq. (2) is different from that usually<sup>16</sup> used (0.269). This is because the area under a close-packed array is not completely covered with atoms.

To estimate the surface area of our specimen, therefore, we take the  $V_m$  value of 0.11 cm<sup>3</sup>/(g of copper) for the argon, together with the value of  $\sigma$  for argon of 11.5 Å<sup>2</sup>, and use Eq. (2) above. The result<sup>‡</sup> is  $\Sigma = 0.374 \text{ m}^2$ /(g of copper), with the monolayer number of argon atoms =  $7.9 \times 10^{18}$  per m<sup>2</sup>.

It should be noted that in deriving Eq. (2), it is implicitly assumed that the underlying metal substrate is smooth. In practice, this cannot be quite true due to flaws, pits, grain boundaries, and various kinds of dislocations. These, in general, will tend to gather more adsorbed atoms than on a smooth surface; hence, it is probable that the  $\Sigma$  value derived using Eqs. (1) or (2) represents an upper bound for the effective surface area for further adsorption after the apparent monolayer number of argon atoms have been adsorbed.

\*This fact is well evidenced, for example, by the absence of diffraction peaks in the scattering of low-energy helium atoms in the experiments of Palmer *et al*.<sup>18</sup>

†A similar structure for monolayers of Xe on graphite surfaces has been shown to occur from LEED experiments by Lander<sup>19</sup> and has been discussed in connection with adsorption by Barnes and Steele.<sup>20</sup>

‡The value for  $\Sigma$  adopted in our previous paper<sup>14</sup> for the same copper specimen (using the  $N_2$  value of  $V_m$ ,  $\sigma(N_2)$  equal to 13.9 Å<sup>2</sup>, and  $\Sigma = 0.269 \sigma V_m$ ) was 0.41 m<sup>2</sup> (g of copper). We suggest that the derived data in that paper obtained using  $\Sigma = 0.41 \text{ m}^2$  (g of copper), be corrected to be compatible with the new value of  $\Sigma$  given herewith, equal to 0.374 m<sup>2</sup> (g of copper).

#### 4. THE HELIUM ADSORPTION ISOTHERMS

The observed adsorption isotherms for  $^4\text{He}$  on the bare copper sponge taken at 18.55, 15.08, 13.50, 11.60, 9.65, 7.90, and 6.18 K are shown in Fig. 1. Those for  $^3\text{He}$ , also on the bare copper sponge, taken at the same temperatures are shown in Fig. 2. Preliminary data on these were given by us<sup>6</sup> previously, which data are now superseded. The amount of gas adsorbed is presented in atoms/ $\text{m}^2$  in the figures.

Little previous data exist for adsorption isotherms of helium on a bare metal with which to compare our data. The early work of Meyer<sup>22</sup> on gold gave two isotherms at 4.21 and 2.04 K, which were at much lower pressures than those reported in this paper, so that no significant comparison can be made.

Our observed adsorption isotherms for  $^4\text{He}$  on a monolayer of argon deposited on the copper [ $2.95 \times 10^{18}$  argon atoms/(g of copper)] taken at 18.55, 15.08, 13.50, 11.60, 9.65, 7.90, and 6.18 K are shown in Fig. 3. Those for  $^3\text{He}$ , also on a monolayer of argon deposited on the copper, taken at the same temperatures are shown in Fig. 4. Preliminary data for the results of Fig. 3 were given by us<sup>6</sup> previously, which data are now superseded.

To provide some comparison with our data, we show in Figs. 3 and 4 data for  $^4\text{He}$  and  $^3\text{He}$  adsorption on a monolayer of argon deposited on

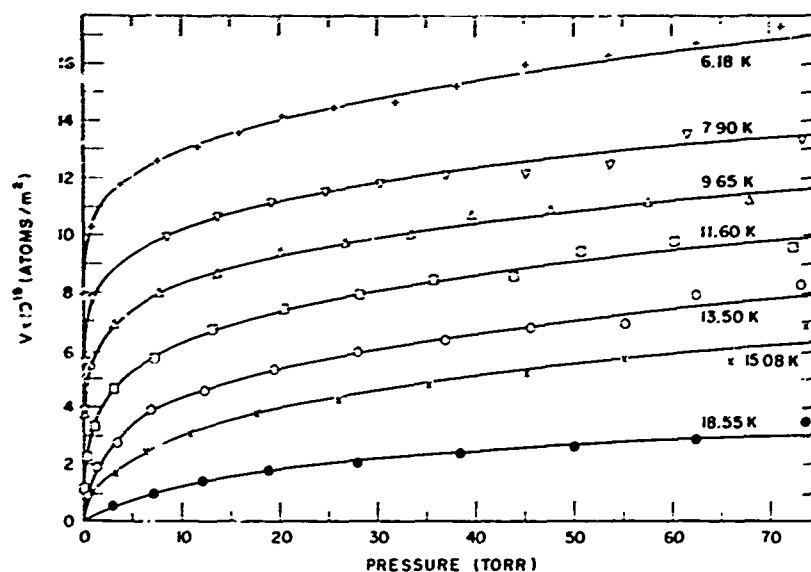


Fig. 1. Adsorption isotherms for  $^4\text{He}$  on bare copper at temperatures as marked



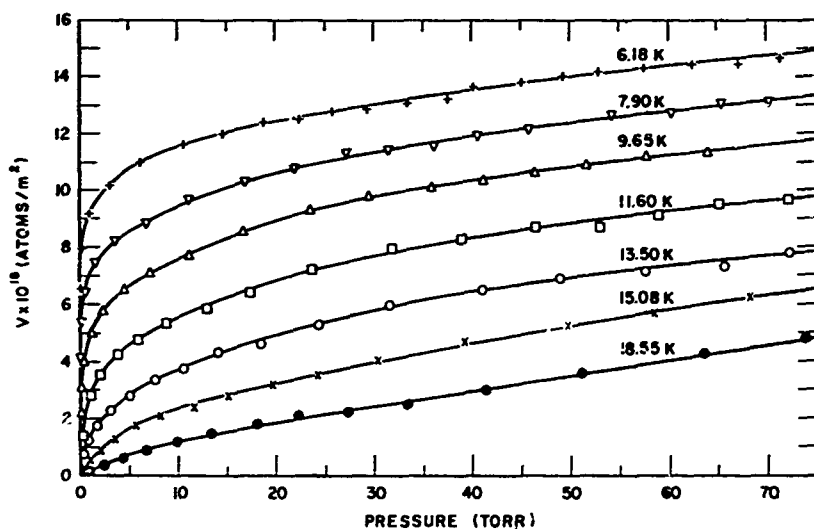


Fig. 2. Adsorption isotherms for  $^3\text{He}$  on bare copper at temperatures as marked.

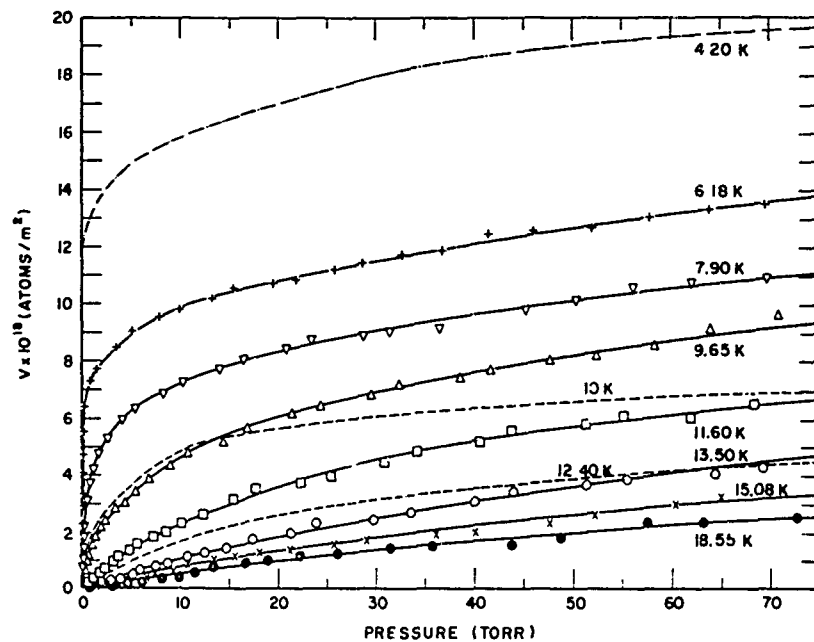


Fig. 3. Adsorption isotherms for  $^4\text{He}$  on a monolayer of argon on copper at temperatures as marked. --- Adsorption isotherm for  $^4\text{He}$  on a monolayer of argon on copper at 4.2 K from McCormick *et al.*,<sup>1</sup> ---- adsorption isotherms for  $^4\text{He}$  on 1.05 layers of argon on  $\text{TiO}_2$  at 10 K and 12.4 K from Steele.<sup>23</sup>

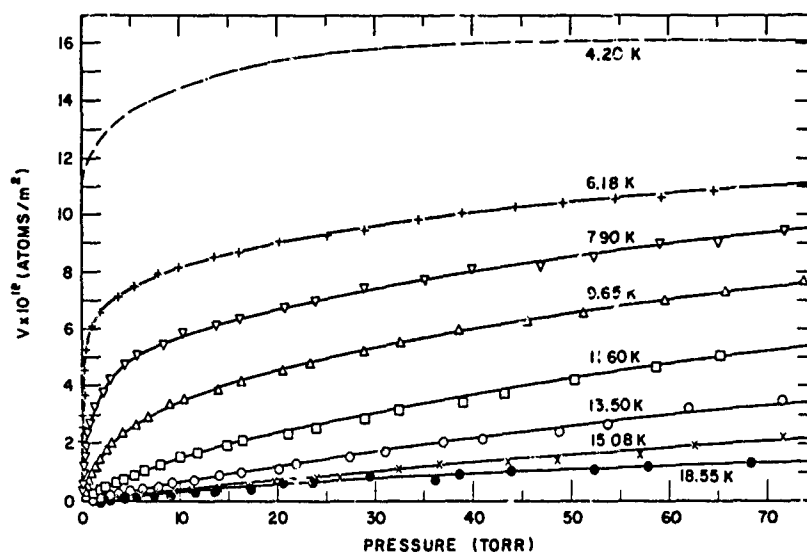


Fig. 4. Adsorption isotherms for  $^3\text{He}$  on a monolayer of argon on copper at temperatures as marked. --- Adsorption isotherm for  $^3\text{He}$  on a monolayer of argon on copper at 4.2 K from McCormick *et al*.<sup>1</sup>

copper at 4.2 K reported by Dash and coworkers.<sup>1</sup> We also show in Fig. 3 data for  $^4\text{He}$  adsorption on a monolayer of argon deposited on  $\text{TiO}_2$  powder at 10.0 and at 12.4 K reported by Steele.<sup>23</sup> Although these earlier measurements were made at different temperatures, and in the case of Steele's<sup>23</sup> data the argon monolayer was deposited on a different substrate, all the experimental data by the different workers are compatible.

The general features of these results are that for the same substrate, the amount of  $^3\text{He}$  adsorbed is always less than that of  $^4\text{He}$  under the same conditions of temperature and pressure. Furthermore, in comparing the adsorption on the argon monolayer with that on the bare copper, the amount adsorbed is always less in the former case than the latter, under the same conditions of temperature and pressure. Indeed, comparison of Figs. 2 and 3 shows that the introduction of an argon monolayer on the copper lowers the adsorption of  $^4\text{He}$ , even below that of  $^3\text{He}$  on the bare copper.

## 5. THE ISOSTERIC HEATS OF ADSORPTION

The large number of adsorption isotherms at different temperatures permit relatively accurate assessment of the isosteric heats of adsorption. Plots of  $\ln p$  vs.  $1/T$  taken from the data of Figs. 1–4 were made at 15 different

constant coverages from  $0.7 \times 10^{18}$  to  $13 \times 10^{18}$  atoms/m<sup>2</sup>. For each coverage there were three or more points, which were colinear, and the slope  $\Delta \ln p / \Delta(1/T)$  gives the isosteric heat of adsorption  $Q_{st}$  divided by the gas constant  $R$ . Figure 5 shows  $Q_{st}/R$  in degrees Kelvin obtained in this way as a function of the coverage for <sup>3</sup>He and <sup>4</sup>He on the bare copper and on the monolayer of argon. (These data supersede the preliminary data previously reported by us.<sup>6</sup>) Figure 5 shows that  $Q_{st}/R$  is significantly lower for adsorption on the argon monolayer than that on the bare copper, both for <sup>3</sup>He and <sup>4</sup>He.

In Fig. 5, a theoretical evaluation of the <sup>3</sup>He and <sup>4</sup>He monolayer coverage is indicated. This is obtained by assuming that the monolayer for both <sup>3</sup>He and <sup>4</sup>He is completed when as many helium atoms are adsorbed as the number of argon atoms in the previously deposited argon monolayer. This theoretical definition will be discussed in detail later in this paper.

The relative flatness of the curves for our data for <sup>3</sup>He and <sup>4</sup>He adsorbed on the argon monolayer indicates considerably more homogeneity of the substrate than is the case for adsorption on bare copper.

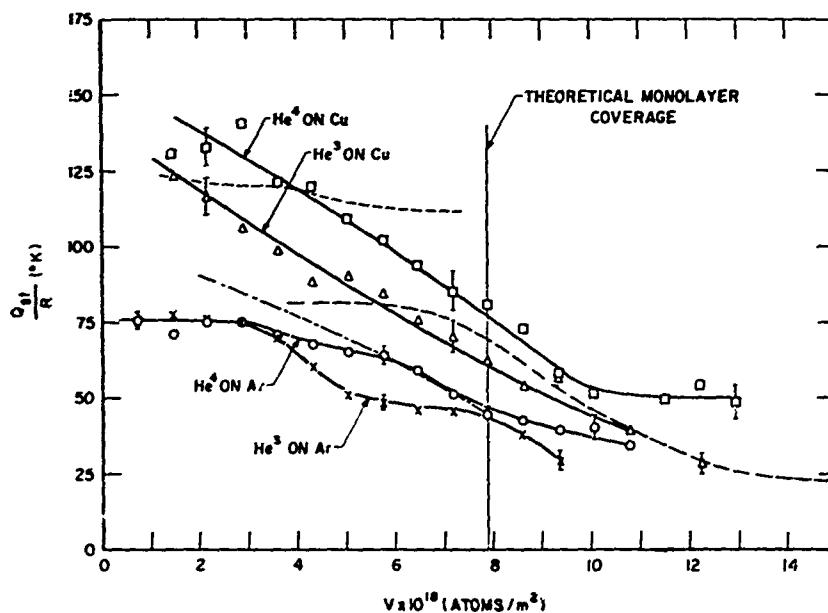


Fig. 5. The isosteric heat of adsorption  $Q_{st}/R$  as a function of coverage for <sup>4</sup>He and <sup>3</sup>He on bare copper and for <sup>4</sup>He and <sup>3</sup>He on a monolayer of argon on copper. — Isosteric heat of adsorption for <sup>4</sup>He on a monolayer of argon on copper from Wallace and Goodstein<sup>7</sup>; --- isosteric heat of adsorption for <sup>3</sup>He on argon from Roy and Halsey<sup>11</sup>; - - - isosteric heat of adsorption for <sup>4</sup>He on 1.05 layers of argon on TiO<sub>2</sub> from Steel and Aston.<sup>2</sup>

Our data indicate that in the limit of zero coverage, the  $Q_{st}/R$  values for  $^3\text{He}$  and  $^4\text{He}$  adsorption on an argon monolayer on copper are  $76 \pm 2$  K for both adsorbates. At the theoretical monolayer coverage on argon, that for  $^3\text{He}$  is  $44 \pm 2$  K and for  $^4\text{He}$ , it is  $47 \pm 2$  K. It is not possible to make an unambiguous extrapolation of  $Q_{st}/R$  to zero coverage for  $^3\text{He}$  or  $^4\text{He}$  adsorbed on the bare copper; it seems clear, however, that the values are relatively high, lying possibly between 135 and 165 K.\* It should be noted here that Pollock *et al.*<sup>24</sup> have determined the binding energy in the limit of zero coverage of  $^4\text{He}$  on bare copper and give a value of 177 K. This would correspond, as deduced from Eq. (3), to a  $Q_{st}/R$  value at 10 K of about 202 K.

At the theoretical monolayer coverage of  $^3\text{He}$  and  $^4\text{He}$  on bare copper, our results give  $Q_{st}/R = 61 \pm 4$  K for  $^3\text{He}$  and  $77 \pm 5$  K for  $^4\text{He}$ .

Previous evaluations of  $Q_{st}/R$  from adsorption isotherms of  $^4\text{He}$  on a monolayer of argon on copper have been made by Wallace and Goodstein,<sup>7</sup> and these data are shown in Fig. 5 for comparison with ours. Included in Fig. 5 also are previous data for  $^4\text{He}$  adsorption on an argon monolayer on  $\text{TiO}_2$  powder reported by Steele and Astor.<sup>27</sup> The  $Q_{st}/R$  in the limit of zero coverage which can be extrapolated from Wallace and Goodstein's<sup>7</sup> data is in close agreement with our value for  $^4\text{He}$ . We felt, however, that this agreement is somewhat fortuitous in view of the very different temperature ranges over which the two different sets of measurements were made. One would anticipate, following Eq. (3), that Wallace and Goodstein's value would fall about 15 K below ours. The data for  $Q_{st}/R$  of Steele<sup>27</sup> for adsorption of  $^4\text{He}$  on an argon monolayer on  $\text{TiO}_2$  is, not too surprisingly, greater than our data by a considerable amount.

## 6. DISCUSSION OF THE HEATS OF ADSORPTION

In order to estimate the heat of adsorption theoretically, a model that has so far received the most attention is one in which the helium adsorbate atom is considered to be held in the van der Waal's field on the surface of a bulk argon crystal [in general, above the (100) face] and interactions between adsorbate atoms are neglected. If  $E_m$  is the maximum depth of the van der Waal's potential at the adsorbent site,  $E_0$  the zero point energy of the adsorbate

\*These values can be compared with that found calorimetrically by Chon *et al.*<sup>25</sup> of 150 K for  $^4\text{He}$  on Platinum Black at  $\theta = 0.3$ . Theoretical estimates of the binding energy for helium on a pure metal can be made, based on calculations of the potential normal to the surface. Many theoretical computations of this potential have been made (see Mavroyannis<sup>26</sup> for a summary of these), which is generally given in the form:  $U = -U_0/z^3$ . To obtain the binding energy  $U_{eq}$ , one supposes that the equilibrium distance is approximately one-half of the sum of the  $^4\text{He}$ - $^4\text{He}$  and the Pt-Pt distances, giving  $z_{eq} = 2.70$  Å. Using this, the values of  $U_{eq}$  are found to range in the major computations cited<sup>26</sup> from 115 to 175 K at  $\theta = 0$  for  $^4\text{He}$  on Pt. Those for  $^4\text{He}$  on Cu would be similar.

atom at the site, and  $E$  the binding energy, then the isosteric heat of adsorption is related to these quantities as follows:

$$|E/k| = |E_m/k| - (E_0/k) = \lim_{\theta \rightarrow 0} (Q_{st}/R) - \frac{1}{2}T \quad (3)$$

where  $\theta$  is the fractional coverage, ( $\theta = 1$  is a monolayer), and  $k$  is the Boltzmann constant.

This model which considers helium adsorption on the (100) face of a bulk argon crystal has been studied by Steele and Ross,<sup>28</sup> Ricca and coworkers,<sup>8</sup> Novaco and Milford,<sup>9</sup> and by Lai, Woo, and Wu.<sup>10</sup> The last authors also considered adsorption on the (111) face of an argon crystal.

Although this model is not directly applicable to our experimental situation in which the argon is only a monolayer on a copper surface, it is of interest to review the final numerical data obtained in these theoretical investigations. These are summed up in Table I. It will be seen that the value of  $|E/k|$  at the adsorbent site is calculated to lie between 93 and 99 K and that the later, more refined calculations do not differ significantly in the resultant  $|E/k|$  values from the early evaluation of Steele and Ross.

No detailed experimental data are as yet available for helium adsorption on argon crystals, although work has been reported by Lee and Gowland<sup>29</sup> on thick argon layers deposited on copper. They found experimentally that  $Q_{st}/R$  in the limit of zero  $^4\text{He}$  coverage on argon deposits of thickness approximately  $2.1 \times 10^{22}$  atoms/m<sup>2</sup> in the temperature range 3–5 K was 205 K. At somewhat higher coverage  $\lim_{\theta \rightarrow 0} (Q_{st}/R)$  fell to about 145 K. These values are considerably larger than the  $|E/k|$  values of Table I. Lee and Gowland suggested that the difference may in part be due to diffusion of the  $^4\text{He}$  into the argon. Pollock *et al.*<sup>24</sup> have made direct measurements of the binding energy  $|E/k|$  by a time-of-flight method for  $^4\text{He}$  adsorption on a thick argon layer (about 20 layers) deposited on copper and found a value of 102 K.

TABLE I  
Results of Calculation of the Binding Energy  $E$  for Helium on the Adsorbent Sites of a Bulk Argon Crystal<sup>a</sup>

Authors	Adsorbent crystal face	Adsorbate atom	$ E_m/k $ , K	$(E_0/k)$ , K	$ E/k $ , K
Steele and Ross <sup>28</sup>	(100)	$^4\text{He}$	188	93.6	94.4
Ricca <i>et al.</i> <sup>8</sup>	(100)	$^4\text{He}$	183	—	—
Novaco and Milford <sup>9</sup>	(100)	$^4\text{He}$	182	83.4	98.6
Lai <i>et al.</i> <sup>10</sup>	(100)	$^4\text{He}$	—	—	93.5
Lai <i>et al.</i> <sup>10</sup>	(111)	$^4\text{He}$	—	—	47.3

<sup>a</sup>Here,  $E_m$  is the value of the potential minimum, and  $E_0$  is the zero-point energy of the adsorbed atom

TABLE II  
Results of Calculation of the Binding Energy  $E$  for Helium on the Adsorbent Sites of an Argon Monolayer Deposited on a Copper Substrate<sup>a</sup>

Authors	Adsorbent	Adsorbate atom	$ E_m/k $	$(E_0/k)$	$ E/k $
Jackson <sup>4</sup>	argon monolayer	$^4\text{He}$	121	54.5	66.5
Novaco and Milford <sup>5</sup>	argon monolayer	$^4\text{He}$	114	51.5	62.5
Novaco and Milford <sup>5</sup>	argon monolayer	$^3\text{He}$	114	56.6	57.4

<sup>a</sup>Here,  $E_m$  is the value of the potential minimum, and  $E_0$  is the zero-point energy of the adsorbed atom.

Theoretical treatments of the case of adsorption of helium on an argon monolayer deposited on a copper substrate have been given by Jackson,<sup>4</sup> and by Novaco and Milford.<sup>5</sup> In the latter treatment, the argon is assumed to be a close-packed array with interatomic distances of 3.84 Å, and both evaluations are made on the basis of *no* interactions between adsorbate atoms. Their final data are given here in Table II.

The experimental data on  $\lim_{\theta \rightarrow 0} (Q_{st}/R)$  and  $|E/k|$  for helium adsorption on an argon monolayer on copper are summed up in Table III, which includes the earlier results of Wallace and Goodstein,<sup>7</sup> as well as those of this paper. The data of Steele and Aston<sup>27</sup> for adsorption on a monolayer of argon on  $\text{TiO}_2$  powder is also given in Table III. By comparison of Tables II and III, it will be seen that the theoretical evaluations of  $|E/k|$  are very close to the experimental results. It is unfortunate that there does not appear to be better agreement between the various experimental data. However, it must be noted here that the term  $\frac{5}{2}T$  in the evaluation of  $|E/k|$

TABLE III  
Experimental Results for  $\lim_{\theta \rightarrow 0} (Q_{st}/R)$  and the Binding Energy  $|E/k|$  for Helium Adsorbed on an Argon Monolayer<sup>a</sup>

Authors	Adsorbent	Adsorbate atom	$\lim_{\theta \rightarrow 0} (Q_{st}/R)$ , K	$T_{av}$ , K	$ E/k $ deduced from Eq. (3), K
This paper	argon monolayer on copper	$^4\text{He}$	76	10	51
This paper	argon monolayer on copper	$^3\text{He}$	76	10	51
Wallace and Goldstein <sup>7</sup>	argon monolayer on copper	$^4\text{He}$	82	4	72
Steele and Aston <sup>27</sup>	argon monolayer on $\text{TiO}_2$ powder	$^4\text{He}$	125	15	87.5

<sup>a</sup>Here,  $T_{av}$  is the average temperature of the measurement

by Eq. (3) plays a significant role for these relatively loosely bound systems. It would therefore be of interest to make further experimental evaluations of  $Q_{\text{ex}}/R$  over wider temperature ranges in order to estimate more exactly its temperature variation.

Roy and Halsey<sup>11</sup> have estimated the coverage variation of  $Q_{\text{ex}}/R$  for <sup>3</sup>He adsorbed on a monolayer of argon on copper from the experimental data of Dash and coworkers.<sup>30</sup> This estimation, based on a patch theory of adsorption, is shown in Fig. 5. It falls close to our data, although, after consideration of the very different temperature range used in Dash *et al.*'s experiment compared to ours, one would expect Roy and Halsey's values to be some 15 K lower than ours. Again, this points up the need for a more thorough investigation of the temperature variation of  $Q_{\text{ex}}/R$ .

## 7. THE MONOLAYER COVERAGE

As remarked in Section 5, a theoretical evaluation of the monolayer coverage has been adopted in Fig. 5, defined as the coverage at which the number of atoms adsorbed (either <sup>3</sup>He or <sup>4</sup>He) is equal to the number of argon atoms in the previously deposited argon monolayer. That is to say, for adsorption on a close-packed array one assumes only one adsorbed atom per unit cell to constitute monolayer coverage. This means that only one-half of the possible adsorption sites are occupied. This definition is frequently used, as for example, by Novaco and Milford,<sup>5</sup> and by Dash and coworkers.<sup>2,3,31</sup>

For adsorption on a close-packed array of argon atoms forming a monolayer on the basic substrate, this definition of monolayer coverage makes  $V_m = 7.9 \times 10^{18}$  atoms/m<sup>2</sup> [ $0.29 \text{ cm}^3 \text{ (STP)/m}^2$ ], if the interatomic distance between argon atoms is taken to be the Lennard-Jones distance  $\rho_0 = 3.83 \text{ \AA}$ .

Experimentally, owing to the possibility of relative mobility of the adsorbate helium atoms (see Novaco and Milford<sup>5</sup>), it is possible that a dynamic adjustment may take place permitting more than  $7.9 \times 10^{18}$  atoms/m<sup>2</sup> in a monolayer, although it is very unlikely that all the adsorption sites can be occupied as a monolayer, as has been suggested by Steele and Ross.<sup>28</sup> Experimental estimates to date of the monolayer capacity of adsorbed helium come from interpretation of adsorption isotherms. In particular, the "Point B" method, or its variants,<sup>16</sup> has been used, which in the case of heliums are subject to some imprecision. The first significant work in these evaluations was that of Meyer<sup>22</sup> for <sup>4</sup>He on gold, who found  $V_m = 13 \times 10^{18}$  atoms/m<sup>2</sup>. A much more definite evaluation was made by Hobson<sup>32</sup> in his elegant very low pressure measurements of <sup>4</sup>He adsorbed on pyrex glass. From his data, one estimates that  $V_m$  ranges between  $8 \times 10^{18}$  and

TABLE IV  
Some Monolayer Capacities of  $^3\text{He}$  and  $^4\text{He}$

Authors	Method	Substrate	Adsorbate atom	Monolayer capacity	
				atoms $\text{m}^{-2}$	$\text{m}^3$ (STP) $\text{m}^{-2}$
This paper	theory	close-packed argon monolayer	$^3\text{He}$ or $^4\text{He}$	$7.9 \times 10^{18}$	0.29
Meyer <sup>22</sup>	expt.	gold	$^4\text{He}$	$13 \times 10^{18}$	0.5
Hobson <sup>12</sup>	expt.	pyrex	$^4\text{He}$	$8.9 \times 10^{18}$	0.30-0.33
Dash <i>et al.</i> <sup>1</sup>	expt.	argon monolayer on copper	$^4\text{He}$	$10.5 \times 10^{18}$	0.39 <sup>a</sup>
Dash <i>et al.</i> <sup>1</sup>	expt.	argon monolayer on copper	$^3\text{He}$	$9.4 \times 10^{18}$	0.35 <sup>a</sup>

<sup>a</sup>See Section 7 for these evaluations.

$9 \times 10^{18}$  atoms/ $\text{m}^2$ . The more recent work of Dash and coworkers,<sup>1</sup> for adsorption on an argon monolayer deposited on copper, yields (according to our interpretations of the surface area  $\Sigma$  of their specimen<sup>23</sup>): for  $^4\text{He}$ ,  $V_m = 10.5 \times 10^{18}$  atoms/ $\text{m}^2$ ; for  $^3\text{He}$ ,  $V_m = 9.4 \times 10^{18}$  atoms/ $\text{m}^2$ . These data are summarized in Table IV. The experimental results for  $V_m$  for adsorption on the argon monolayer, therefore, appear to be somewhat larger than the theoretical definition. The fact that  $V_m$  for  $^4\text{He}$  on pyrex glass is numerically so similar to that which one estimates theoretically for adsorption on a close-packed argon layer indicates that on pyrex the monolayer of  $^4\text{He}$ , if it is also close packed, has interatomic spacing of about 3.8 Å.

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#### REFERENCES

1. W. D. McCormick, D. L. Goodstein, and J. G. Dash, *Phys. Rev.* **168**, 249 (1968).
2. G. A. Stewart and J. G. Dash, *Phys. Rev.* **A2**, 918 (1970).
3. G. A. Stewart and J. G. Dash, *J. Low Temp. Phys.* **5**, 1 (1971).
4. H. W. Jackson, *Phys. Rev.* **180**, 184 (1969).
5. A. D. Novaco and F. J. Milford, *Phys. Rev.* **A4**, 1136 (1971).

<sup>a</sup>Using the "standard" method, with  $\sigma(\text{N}_2) = 16.2 \text{ Å}^2$ , Dash and coworkers<sup>1</sup> quote an area for their specimen of  $55 \text{ m}^2$ . If one follows our procedure given in Section 3, with  $\sigma_{\text{argon}} = 11.5 \text{ Å}^2$  and notes that their argon monolayer coverage is  $11.9 \text{ cm}^3$  (STP), then use of Eq. (2) above yields  $\Sigma = 40.5 \text{ m}^2$ . Using the data of their Table I, then for  $^4\text{He}$ ,  $V_m = 0.39 \text{ cm}^3$  (STP)  $\text{m}^2$  and for  $^3\text{He}$ ,  $V_m = 0.35 \text{ cm}^3$  (STP)  $\text{m}^2$ .



6. J. G. Daut and E. Lerner, *Proc. of 2nd International Symp. on Adsorption Desorption Phenomena*, Florence 1971, Academic Press.
7. J. L. Wallace and D. L. Goodstein, *J. Low Temp. Phys.* 3, 283 (1970).
8. F. Rizza, C. Pisani, and E. Garrone, *J. Chem. Phys.* 51, 4979 (1969).
9. A. D. Novaco and F. J. Milford, *J. Low Temp. Phys.* 3, 397 (1970).
10. H.-W. Lai, C.-W. Woo, and F. Y. Wu, *J. Low Temp. Phys.* 5, 499 (1971); 3, 463 (1970).
11. N. N. Roy and G. D. Halley, *J. Low Temp. Phys.* 4, 231 (1971).
12. P. Mahadev, M. F. Penczyk, R. A. Scribner, and J. G. Daut, to be published.
13. J. G. Daut and C. Z. Rosen, *J. Low Temp. Phys.* 3, 89 (1970).
14. E. Lerner and J. G. Daut, *J. Low Temp. Phys.* 6, 241 (1972).
15. D. L. Goodstein, W. D. McCormick, and J. G. Dash, *Cryogenics* 6, 167 (1966).
16. D. M. Young and A. D. Crowell, *Physical Adsorption of Gases* (Butterworths, London, 1962).
17. W. A. Steele, *J. Low Temp. Phys.* 3, 251 (1970).
18. R. L. Palmer, D. R. O'Keeffe, H. Saltsberg, and J. N. Smith, *J. Vac. Sci. Technol.* 7, 91 (1970).
19. J. J. Lander, *Proc. Symp. Gas Surface Interactions*, San Diego, Dec. 1966, H. Saltsberg et al., eds. (Academic Press, New York, 1967), p. 25.
20. M. Barnes and W. A. Steele, *Proc. Symp. Gas Surface Interactions*, San Diego, Dec. 1966, H. Saltsberg et al., eds. (Academic Press, New York, 1967), p. 243.
21. A. C. Hollis-Naile, *Argon, Helium and the Rare Gases*, (Interscience, New York, 1961), p. 313.
22. L. Meyer, *Phys. Rev.* 103, 1593 (1956).
23. W. A. Steele, *J. Phys. Chem.* 61, 1551 (1957).
24. F. Pollock, H. Logan, J. Hobgood, and J. G. Daut, *Phys. Rev. Letters* 28, 346 (1972).
25. H. Chou, R. A. Fisher, R. D. McCammon, and J. G. Aston, *J. Chem. Phys.* 36, 1378 (1962).
26. C. Mavroyannis, *Molecular Physics* 6, 593 (1963).
27. W. A. Steele and J. G. Aston, *J. Amer. Chem. Soc.* 79, 2393 (1957).
28. W. A. Steele and M. Ross, *J. Chem. Phys.* 35, 850, 262 (1961).
29. T. J. Lee and L. Gouland, *Proc. 2nd International Symp. on Adsorption Desorption Phenomena*, Florence 1971, Academic Press.
30. J. G. Dash, R. E. Peierls, and G. A. Stewart, *Phys. Rev.* A2, 932 (1970).
31. J. G. Dash and M. Bretz, *Phys. Rev.* 174, 247 (1968).
32. J. P. Hobson, *Can. J. Phys.* 37, 500 (1959).

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## TRANSITIONS IN NEON SUBMONOLAYERS ADSORBED ON ARGON-COATED GRAFOIL\*

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# TRANSITIONS IN NEON SUBMONOLAYERS ADSORBED ON ARGON-COATED GRAFOIL\*

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Adsorption isotherms of neon on Grafoil and on argon-coated Grafoil have been measured between 17 K and 27 K. For the argon-coated substrate, evidence appeared for a transition of the neon into a mobile two-phase system with critical temperature 21.5 K.

Adsorption isotherms of submonolayers of neon on exfoliated graphite ("Grafoil") [1] coated with a monolayer of argon, have been measured, this substrate having been found previously [2] to be a relatively homogeneous. The measurements were made using an apparatus and a method which has been previously described by us [3]. The Grafoil substrate was 0.013 cm thick, 1.9 cm wide, wound in a cross-packed helix of mass 33.61 g. Its surface area, deduced from an argon adsorption isotherm [2] at 77.3 K, was 672 m<sup>2</sup>. The argon monolayer was uniformly deposited on the Grafoil before measurement of the neon isotherms was begun. Neon adsorption isotherms were measured at 17.26 K, 20.22 K, 27.64 K, 25.71 K and 27.00 K and are shown in fig. 1 (a). Fig. 1 (a) shows estimates of the monolayer coverage: the theoretical monolayer coverage of  $7.9 \times 10^{18}$  atoms/m<sup>2</sup> being that corresponding to a close-packed surface layer [4] and the other estimate of  $10 \times 10^{18}$  atoms/m<sup>2</sup> being that of Antoniou et al. [5] on graphitized carbon (Spheron 6).

Fig. 1 (a) indicates that a transition occurs in the range of our observations, the curves being similar in character to those observed, for example, by Fisher and McMillan [6] for krypton on NaBr. At the lower pressures we interpret our data to mean that at submonolayer coverage two phases exist simultaneously. If as a first approximation, we interpret our data in terms of a van der Waals 2-D system, in the same way that Ross and Winkler did for argon on graphite [7],

we obtain a critical temperature of 21.5 K.

The specific heat measurements of submonolayers ( $\theta = 0.5$ ) of neon on graphitized carbon (Spheron 6) by Steele and Karl [8] and by Antoniou et al. [5] showed anomalies with maxima at 16.1 K and 14 K respectively, which were interpreted as due to a "melting", over a temperature range, of the adsorbate. Although a quantitative comparison of these results with our data is not possible, due to the differences in the substrates, it seems evident that both our adsorption and their calorimetric experiments suggest that these submonolayers are two phase systems.

By interpreting our isotherm data in terms of a modified Fowler isotherm, as has been done by Fisher and McMillan [6], we conclude that the neon-neon lateral interaction energy is approximately 58 K.

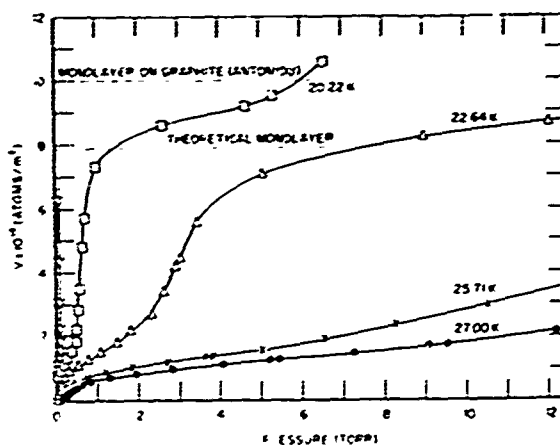


Fig. 1 (a) Adsorption isotherms for neon on argon-coated Grafoil at temperatures as marked. points  $\nabla$  are for 17.26 K.

\* Work partially supported by a Grant from the National Science Foundation and by contracts with ONR and DOD (Themis Program)

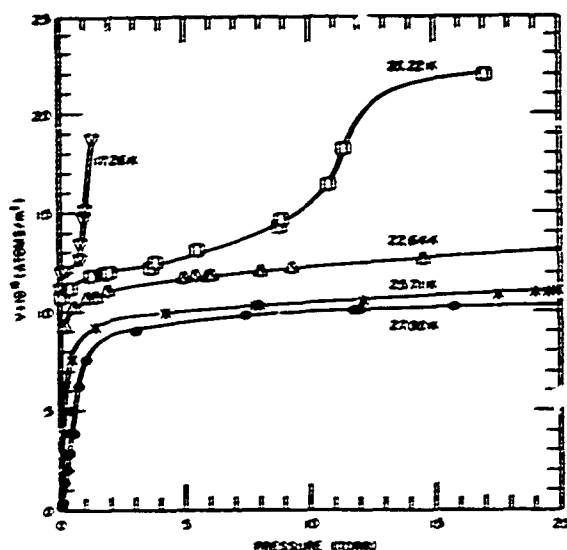


Fig. 1. b) Adsorption isotherms for neon on Grafoil at temperatures as marked.

We have also observed adsorption isotherms for neon on bare Grafoil, as shown in fig. 1 (b). The two (at 25.71 K and 27.00 K) or perhaps three (one at 22.64 K) isotherms which are mostly below monolayer coverage show no evidence of a transition in the system. The marked steps observed in the 17.26 K and 20.22 K isotherms above monolayer coverage are indicative of second layer formation. We have computed the isosteric heat of adsorption ( $Q_{st}/R$ ) in the usual way [9] from our data and the results, as a function of the coverage, are shown in fig. 2. Fig. 2 also shows for comparison ( $Q_{st}/R$ ) observed by Antoniou et al. [5] for neon on Spheron 6 at 29 K.

We wish to thank Mr. W.H.P. Van Iperen, for his help in the experiments.

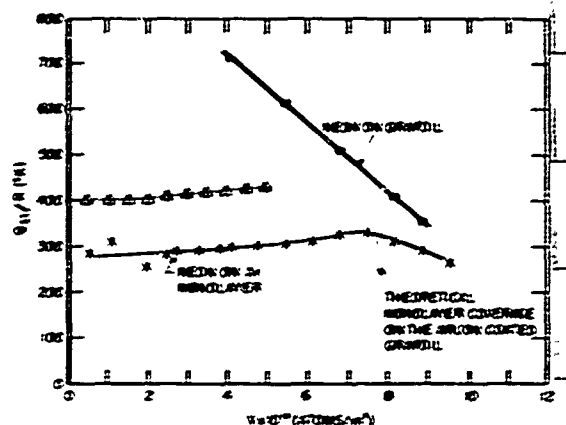


Fig. 2. The isosteric heat of adsorption  $Q_{st}/R$  as a function of coverage for neon on bare Grafoil and on a monolayer of argon on Grafoil: points  $\Delta$  are isosteric heats of adsorption of neon on graphitized carbon by Antoniou et al.

### References

- [1] "Grafoil", manufactured by Union Carbide Carbon Products Division, 270 Park Ave., New York.
- [2] E. Lerner and J.G. Daunt, *J. Low Temp. Phys.*, to be published.
- [3] J.G. Daunt and C.L. Rozen, *J. Low Temp. Phys.* 3 (1970) 89.
- [4] J.G. Daunt and E. Lerner, *J. Low Temp. Phys.* 8 (1972) 1.
- [5] A.A. Antoniou, P.D. Scaife and J.M. Peacock, *J. Chem. Phys.* 54 (1971) 5403.
- [6] B.B. Fisher and W.G. McMullan, *J. Am. Chem. Soc.* 79, (1957) 2969; *J. Chem. Phys.* 28 (1956) 547, 555, 562.
- [7] S. Ross and W. Winkler, *J. Colloid Sci.* 10 (1955) 319, 330.
- [8] W.A. Steele and R. Karl, *J. of Colloid and Interface Science* 26 (1968) 397.
- [9] W.M. Young and Crowell, *Physical adsorption of gases* (Butterworths, London 1962).

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**THE SPECIFIC HEATS OF SUBMONOLAYERS OF  $^4\text{He}$  ADSORBED ON COPPER  
AND ON ARGON AND NEON MONOLAYERS ON COPPER AT LOW TEMPERATURES\***

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pp. 221-222



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# THE SPECIFIC HEATS OF SUBMONOLAYERS OF $^4\text{He}$ ADSORBED ON COPPER AND ON ARGON AND NEON MONOLAYERS ON COPPER AT LOW TEMPERATURES\*

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Specific heats of  $^4\text{He}$  adsorbed on copper, on argon-coated copper and on neon-coated copper have been measured between 0.6K and 4K. Near monolayer coverages the films show two dimensional Debye behavior. At lower coverages, down to 0.14 monolayers, the specific heat per atom is anomalous and is unexplained by any single phase model of the adsorbed system.

We have measured the specific heat of adsorbed submonolayers of  $^4\text{He}$  deposited on three substrates, namely: 1) bare copper, 2) copper coated with a monolayer of argon and 3) copper coated with a monolayer of neon. The copper was a sintered sponge [1] of mass 695 g and total surface area, as previously determined [2,3], 260 m<sup>2</sup>. It was located in an adiabatic calorimeter. The same calorimeter and sponge was used for substrates 2) and 3), the argon and neon monolayers being put down before cooling to liquid helium temperatures. Measurements were made with each of the three different substrates at  $^4\text{He}$  fillings of the calorimeter in amounts 15, 30, 50, 60, 70 and 87.5 cm<sup>3</sup> (STP).

The results for substrates 1) and 2) extend and largely confirm previous data of Princehouse [4] for bare copper and of Stewart and Dash [5] for argon-coated copper.

The specific heat,  $C$ , for near-monolayer coverage of  $^4\text{He}$  on all three substrates could be described by the addition of two terms: one a two-dimensional (2-D) Debye function, and the other due to the evaporation of  $^4\text{He}$  from the adsorbed film into the 3-D vapor. At least for substrate 2), where the effective binding energy,  $E'$ , is approximately coverage independent, the evaporation term can be evaluated [6] from theory.

Typical results from our data for a coverage,  $x = 0.93$  monolayers, on substrate 2) are shown by the circled points in fig. 1. The full curve is a theoretical

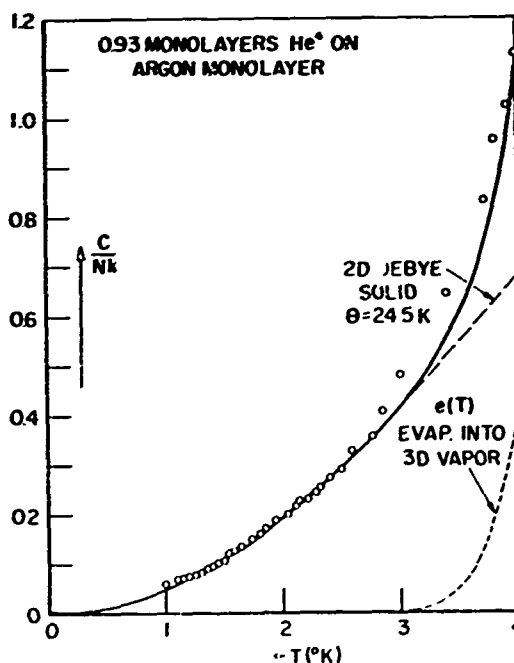


Fig. 1.

one obtained with  $\theta = 24.5\text{K}$  in the 2-D Debye function and with  $E' = 61.5\text{K}$  in the evaporation term [6]. Satisfactory agreement is evident. Moreover the value of  $E'$  is in agreement with that obtainable in other theoretical and experimental evaluations [3]. It is found that Stewart and Dash's [4] data for the specific heat of  $^3\text{He}$  on argon-coated copper, with coverage  $x = 0.9$ , can also be well described by these two terms with  $\theta = 26.5\text{K}$  and  $E' = 61.5\text{K}$ . Our results for near-monolayer coverage on the bare copper also can be described

\* Supported in part by a grant from the National Science Foundation and by contracts with ONR and DOD (Themis Program).

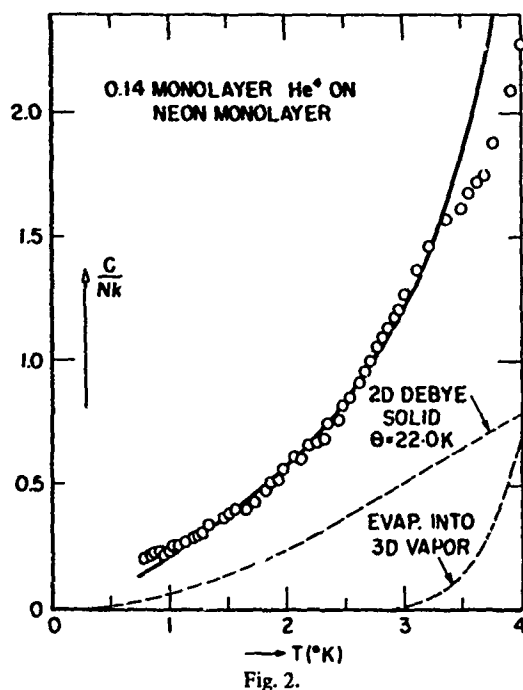


Fig. 2.

in a similar way with  $\theta = 28.3\text{K}$  for  $x = 0.85$  and  $\theta = 30.0\text{K}$  for  $x = 1.07$ .

For the neon-coated copper, the near-monolayer coverage ( $x = 0.8$ ) film also showed a 2-D Debye behaviour below about 2 K, with  $\theta = 22.0\text{K}$ .

At coverages below the monolayer coverage, the specific heat per adsorbed atom increases with decreasing coverage at any temperature below about 2.5 K. Illustrating this fig. 2 shows the specific heat per

atom for  $x = 0.14$  on the neon-coated substrate. Fig. 1 of the subsequent letter [6], gives our results for  $x = 0.2$  on the argon monolayer. In these figs. curves for the 2D Debye solid and for the 3-D evaporation term, with their appropriate  $\theta$  and  $E'$  values have been included and they clearly show that the sum of these two terms alone does not describe the low coverage results.

It has not been found possible to account for the low coverage results by any homogeneous single phase model [7] of the adsorbed system, whether gaseous or condensed, nor by a solid two-patch model as proposed by Stewart and Dash [5]. It has been found [6], however, that a two-phase model can describe the results qualitatively and, at least for substrates 2) and 3) quantitatively. The full curves of fig. 2 and of fig. 1 of ref. [6] were computed using this two-phase model.

#### References

- [1] D.L. Goodstein, W.D. McCormick and J.G. Dash, *Cryogenics* 6 (1966) 167.
- [2] E. Lerner and J.G. Daunt, *Jour.Low Temp.Phys.* 6 (1972) 241.
- [3] J.G. Daunt and E. Lerner, *Jour.Low Temp.Phys.* 8 (1972) 79.
- [4] D.W. Princehouse, *J.Low Temp.Phys.*, to be published.
- [5] G.A. Stewart and J.G. Dash, *Phys.Rev.A2* (1970) 918.
- [6] J.G. Daunt, *Phys.Lett.* 41A (1971)
- [7] F.J. Milford and A.D. Novaco, *Phys.Rev.A41* (1971) 1136.

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## **SOME PROPERTIES OF TWO PHASE SUBMONOLAYERS OF ADSORBED HELIUM\***

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## SOME PROPERTIES OF TWO PHASE SUBMONOLAYERS OF ADSORBED HELIUM\*

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A two phase model for helium submonolayers adsorbed on argon and neon monolayers is proposed which consists of two-dimensional (2-D) solid-like islands, of coverage independent lattice parameter, surrounded by a quasi-ideal 2-D vapor. This model can approximate the observed specific heats of such submonolayers provided an anomalous term is introduced which may be associated with those atoms located around the perimeters of the islands.

A two-phase model, with one phase a mobile 2-D gas, is considered to explain the specific heats given in the previous letter [1]. The model [2] assumes that the adsorbate forms solid-like two-dimensional (2-D) islands, surrounded by a quasi-ideal 2-D vapor. The island atoms are assumed to be in register with the substrate, regardless of their total number. This system, at fractional coverage  $x$  ( $x=1$  is a completed monolayer) has these terms in its specific heat:

1) A 2-D lattice term, due to vibrations in the islands, which is assumed to be a 2-D Debye function, i.e.  $C_1/Nk = D(T/\theta)$ , with  $\theta$  independent of  $x$  and with  $\theta \propto m$ .

2) A desorption term, due to evaporation into the 3-D voids above the surface, in which is included a small term due to the specific heat of the 3-D vapor. By extending the theoretical work of Fisher and McMillan [3] on the 3-D vapor pressure to a two-phase system, term 2) gives, at sufficiently low temperatures, a specific heat per atom:

$$\frac{C_2}{Nk} = \left[ \frac{(2\pi m)^{3/2} k^{5/2}}{h^3} \right] \frac{V}{n_m R} \left( \frac{1}{1-x} \right) T^{1/2} \times$$

$$\times \left[ E' + \frac{3}{2} T \right]^2 + \frac{3}{2} T^2 \exp\left(-\frac{E'}{T}\right) \quad (1)$$

where  $V$  is the 3-D vapor volume in the calorimeter,  $n_m$  the number of moles in a helium monolayer in the calorimeter and where  $E'$  is the effective binding

\* Supported in part by a grant from the National Science Foundation and by contracts with ONR and DOD (Themis Program)

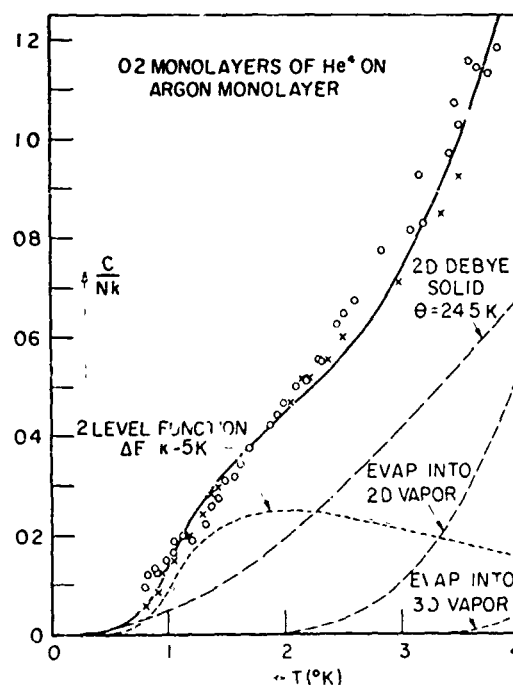


Fig. 1.

energy, being equal to the binding energy for zero coverage less the adsorbate pair interaction energy [4]. Note that  $C_2$  is proportional to  $1/(1-x)$  and to  $m^{3/2}$ .

3) A desorption term, due to evaporation from the islands into the 2-D vapor in which a small term due to the 2-D vapor itself is included. This yields a specific heat per particle:

$$\frac{C_3}{Nk} = \left[ \frac{2\pi m k^2}{h^2} \right] \frac{A}{n_m R} \left( \frac{1-x}{x} \right) T^{-1} \{ (E_2 + T)^2 + T^2 \} \times \\ \times \exp(-E_2/T) \quad (2)$$

where  $A$  is the total surface area in the calorimeter and  $E_2$  is the lateral (2-D) binding energy of an atom at the perimeter of an island. Note that  $C_3$  is proportional to  $(1-x)/x$  and to  $m$ .

4) A 1-D lattice term, due to vibrations around the perimeters of the islands. This yields a negligible small contribution.

5) An 'anomalous' term, perhaps due to one or more of the following. a) Transitions between sites of different energies around the 'fretted' edges of the islands, which would give a term proportional to the perimeter, b) Transitions between different areal configurations, assuming some distortion in the 2-D lattices; c) following Roy and Halsey [5], terms due to distributions among heterogeneous sites of long range potential variation.

We have applied this model to the specific heat data [1,6] for  $^3\text{He}$  and  $^4\text{He}$  on argon and neon monolayers on copper and have found that, at low coverages, the sum of 1) through 3) does not completely represent the data. There remains the anomalous term. As an illustration of this, fig. 1 shows the experimental data points (o for Mahadev et al. [1], X for Stewart and Dash [6]) together with curves showing terms 1), 2) and 3) separately for 0.2 monolayers  $^4\text{He}$  on an argon monolayer on copper. The full curve, roughly agreeing with experiment, was obtained by adding the curves for terms 1), 2), and 3), together with a two-level Schottky function with energy gap  $\Delta E/k = 5\text{K}$ . We have taken a two-level function to be a first approximation for the 'anomalous' term. Thus we find that we can describe the experimental results by summing four terms, a process which introduces five assignable variables:  $\theta$ ,  $E'$ ,  $E_2$  and  $\Delta E$  and the maximum value of the two-level function. It has been found that for five

different coverages [1] of  $^4\text{He}$  on the argon monolayer, all the experimental data can be accounted for using the same values of four of these variables, namely  $\theta = 24\text{K}$ ,  $E' = 61.5\text{K}$ ,  $E_2 = 21.5\text{K}$  and  $\Delta E/k = 5\text{K}$  and with a variation of the maximum value of the two-level function proportional to  $1/x^{1/2}$ . This proportionality is suggestive of a mechanism associated with those atoms located around the perimeters of the islands. It is noted that the values of  $E'$  and  $E_2$  are consistent with previous estimates of these terms from other data [6-8]. Furthermore, with a change only in  $\theta$  from 24.5 K for  $^4\text{He}$  to 26.5 K for  $^3\text{He}$ , the same values of the other parameters account very satisfactorily for the observed specific heats of four different coverages [6] of  $^3\text{He}$  on argon. In addition for three different submonolayer coverages of  $^4\text{He}$  on the neon monolayer [1] the same situation holds, namely all the specific heat data can be approximated by the model with the following values of the parameters;  $\theta = 22.0\text{K}$ ,  $E' = 46.0\text{K}$ ,  $E_2 = 16.0\text{K}$  and  $\Delta E/k = 5\text{K}$ , and with the maximum value of the two-level function the same as that for the argon substrate at equivalent coverage.

I wish to thank Dr. P. Mahadev for his help and Drs. F. Pollock and A.D. Novaco for valuable discussions.

#### References

- [1] P. Mahadev, M.F. Panczyk, R.A. Scribner and J.G. Daunt, Phys. Letters 41A (1972) 221.
- [2] J.G. Daunt, Bull. Amer. Phys. Soc. 17 (1972) 498.
- [3] B.B. Fisher and W.G. McMillan, J. Chem. Phys. 28 (1958) 555.
- [4] R.H. Fowler and E.A. Guggenheim, Statistical thermodynamics, (Cambr Univ. Press, New York, 1939).
- [5] N.N. Roy and G.D. Halsey, J. Low Temp. Phys. 4 (1971) 231.
- [6] G.A. Stewart and J.G. Dash, Phys. Rev. A2 (1970) 918.
- [7] A.D. Novaco and F.J. Milford, Phys. Rev. A41 (1971) 1136.
- [8] J.G. Daunt and E. Lerner, J. Low Temp. Phys. 8 (1972) 79.



Two cryostats were built for desorption cooling in the temperature range below 12 K, using desorption of  $\text{He}^4$  gas from synthetic zeolite. The desorption cooling experiments carried out with these cryostats are described. The initial temperatures chosen were 12.0 K, 10.0 K, 8.0 K, and 6.0 K and initial pressures between 0.25 atm and 1.00 atm (1 atm = 101 kN m<sup>-2</sup>). Final temperatures ranged down to 1.83 K. Measurements were made of the rate of warm-up under various power loadings (powers up to 12.8 mW were employed) at the final low temperatures and the results, as a function of the average temperature, are presented. With the larger cryostat, containing 130 g of synthetic zeolite refrigeration was maintained for periods longer than 25 hours. An assessment is made on the limitations of the cooling process based on the results reported here and on previous experiments on adsorption isotherms. Data are presented in tabular form for the expected duration of refrigeration and total refrigerative capacity at various temperature levels from 3.0 K to 6.0 K for 1 kg of synthetic zeolite; as an example, this would permit refrigeration to be maintained between 4.0 K and 5.0 K for 130 hours for a 1 mW power loading.

## Desorption cooling below 12 K using $\text{He}^4$ desorbed from synthetic zeolite

J. G. Daunt and C. Z. Rosen

The experimental investigations reported here were undertaken in a study of the potential application of desorption cooling as a second stage for further lowering of temperature in miniaturized refrigeration systems. Desorption cooling offers some advantages, especially in simplicity, for maintaining temperatures in the range 2 K to 10 K, starting from temperatures readily produced by mechanical refrigerators<sup>1</sup> or solid hydrogen packs.<sup>2</sup>

The method is well-known, having been devised many years ago by Simon<sup>3</sup> and used for helium liquefaction by Mendelssohn<sup>4</sup> as early as 1931. Moreover, some experimental studies of the performance of desorption cooling systems in the temperature range below 20 K using activated charcoal as the adsorbent were made some time ago by van Itterbeek and van Dingenen<sup>5</sup> and by Kanda.<sup>6</sup> More recently Bewilogua and Reichel<sup>7</sup> have reported similar experimental studies at higher temperatures (40–70 K) using silica gel as the adsorbent. Some of our preliminary results on desorption cooling using various adsorbents, namely: charcoal, silica gel, alumina, and synthetic zeolite, have already been reported<sup>8,9</sup> by one of us (JGD). These results indicated that synthetic zeolite (Linde Molecular Sieve, type 13X) was a more favourable material for desorption cooling, using  $\text{He}^4$  as the working gas, in the temperature range 2 K to 10 K than many others. A more detailed experimental study, therefore, of desorption of  $\text{He}^4$  from synthetic zeolite seemed justified and the results are presented below. In the meantime we have published<sup>10,11</sup> detailed

measurements of the adsorption isotherms of  $\text{He}^3$  and  $\text{He}^4$  on synthetic zeolite 13X in the temperature range 4.2 K to 20 K, together with the deduced equilibrium thermodynamic data. The latter are of value in interpretation of the present desorption experiments.

A description of the synthetic zeolite adsorbent together with details of its preparation is given in section 1. Section 2 describes the experimental arrangements and procedures. The latter covered not only measurement of the final pressures ( $p_f$ ) reached from a variety of initial temperatures ( $T_i$ ) and pressures ( $p_i$ ) but also covered extended measurements of the maintenance of the low temperatures for periods up to 25 hours. During these extensive runs, heat was applied electrically in various measured amounts up to about 13 mW to the desorbed sample cell and the resulting warming rates recorded. Data from many of these runs are reported in section 3 together with other pertinent experimental results that were obtained.

Section 4 discusses the results in detail, presents an interpretation of the physical processes determining the desorption coolings and the refrigeration capacities, and provides in tabular form engineering data for future design

### 1. Details of the adsorbent and its preparation

The synthetic zeolite which was used in our experiments as adsorbent was obtained from the Linde Division of Union Carbide Corporation and is referred to as 'Molecular Sieve 13X'. The chemical composition of a hydrated unit cell is given by  $\text{Na}_{86}[(\text{AlO}_2)_{86}(\text{SiO}_2)_{106}] \cdot 276\text{H}_2\text{O}$ . It

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**Table 1. Data on content by volume of zeolite 13X pellets having 2% by weight of water. (From Mr F. Harris,<sup>16</sup> private communication)**

Volume	% of pellet volume
Intracrystal void	28.1
Solid portion of crystal	29.3
Solid portion of binder	9.3
Inter-crystal void	33.4

consists of  $\text{SiO}_4$  and  $\text{AlO}_4$  tetrahedra which build up structural units of truncated octahedra, called  $\beta$ -cages<sup>12,13,14</sup> of interior diameter 6.6 Å. The  $\beta$ -cages are tetrahedrally arranged and there are 8  $\beta$ -cages in a unit cell. The tetrahedral framework of the  $\beta$ -cages enclose larger polyhedral cavities called  $\alpha$ -cages<sup>13,15</sup> having a free diameter of about 11.8 Å. There are 8  $\alpha$ -cages per unit cell, which is a cube of side 24.95 Å. The 8  $\alpha$ -cages and 8  $\beta$ -cages per unit cell provide an intracrystal void volume of  $8\,080\text{ Å}^3$ , or about 50% of the total volume of the crystal.

Pellets of zeolite 13X were used in the experiments reported here. They were specified to contain 20% by weight of an 'inert clay binder'. They were approximately  $\frac{1}{4}$  in (6.4 mm) long and  $\frac{1}{16}$  in (1.6 mm) in diameter. The partially dehydrated pellets used contained about 2% by weight of water and had a density of about  $1.0\text{ g cm}^{-3}$ ; this water is necessary to prevent structural distortion.<sup>16</sup> The different volumes occupied by the crystals and the binder<sup>16</sup> are noted in Table 1 taking one pellet as the basis for 100% of the volume.

In both the cryostats used in our experiments, each desorption cell was first filled with pellets to its maximum capacity. In doing this, an electric vibrator was used to maximize the filling. Then this filling of zeolite was removed and dried in a vacuum oven at  $110^\circ\text{C}$  for over 24 hours. It was then weighed in a covered weighing bottle at room temperature. An identical heating and weighing procedure was repeated several times until there was no further weight change. The final weight of the filling for the first (small) cryostat (System A) was 3.53 g, which corresponded to a pellet density of about  $1.08\text{ g cm}^{-3}$ . This treated and measured quantity of zeolite was then replaced in the desorption cell. The weight of the pellets for the second cryostat (System B) was measured after an identical procedure and was 129.6 g.

After the above procedure of filling each desorption cell, the following preparatory treatment was carried out before experiments began: (1) high-vacuum pumping at  $60^\circ\text{C}$  for several hours, (2) high-vacuum pumping at room temperature for more than 48 hours, (3) purging several times with dry  $\text{He}^4$  gas at room temperature, and (4) high vacuum pumping at room temperature for more than 48 hours. It is noted that purging with the adsorbate is recommended by Brunauer<sup>17</sup> to be one of the most effective methods of purifying the surface.

Furthermore, between each desorption run we adopted a routine of high vacuum pumping of the desorption cell at room temperature for 48 hours in order to assure reproducibility of our data.

## 2. Experimental arrangements and procedures

Two desorption apparatus were used in the experiments, a small scale one (System A) containing 3.53 g of 13X adsorbent and a larger one (System B) containing 129.6 g of 13X adsorbent.

System A is described first. In it, the adsorbent was contained in a desorption cell,  $V_1$ , comprising a copper vessel of internal volume  $5.70\text{ cm}^3$  and mass 24.2 g to which was attached a calibrated germanium resistance thermometer (Solitron, type No 2401), a  $100\ \Omega$  heater comprising a bifilarly wound  $\frac{1}{8}$  W No 32 Evanohm wire and a 2.8 mm id thin walled stainless steel filling and exhaust tube which led to the room temperature part of the cryostat. The vessel  $V_1$  was located within an inner vacuum vessel,  $V_2$ , which in turn was located within an outer vacuum vessel  $V_3$ . The outer vessel  $V_3$  was immersed in a liquid  $\text{He}^4$  bath at 4.2 K and could be evacuated to high vacuum.

The inner vacuum vessel,  $V_2$ , was equipped with two calibrated germanium resistance thermometers, (same type as on  $V_1$ ), a 200  $\Omega$  heater (similar to that on  $V_1$ ). One resistance thermometer and the heater were connected to an electronic temperature controller by means of which  $V_2$  could be maintained at any desired preset temperature between 4.2 K and 80 K with a long term precision of  $\pm 0.003\text{ K}$ . By having initially exchange gas in  $V_2$ , the desorption cell  $V_1$  could be filled with  $\text{He}^4$  gas at any desired initial temperature in the above mentioned temperature range. Before starting a desorption run,  $V_2$  would be highly evacuated in order to isolate  $V_1$  thermally from its surroundings.

System B, with the larger amount of adsorbent, incorporated a larger diameter tube for pumping on the desorption cell and a separate tube for measurement of the pressure in the cell. It incorporated otherwise similar general qualitative arrangements as System A and it is sketched in Fig.1. The significant differences were as follows: the desorption cell,  $V_1$ , was a cylinder of copper with internal dimensions 10.2 cm long and 5.1 cm id and weighing 386 g. The pumping tube connected to  $V_1$  was 0.90 cm id and 5.0 cm long between  $V_1$  and  $V_2$  (see Fig.1), 1.85 cm id and 48.0 cm between  $V_2$  and the 60 K level, where it enlarged to 3.68 cm id to the top flange of the cryostat. It contained two radiation baffles, as shown in Fig.1. Above the top flange it enlarged to 5.1 cm id and led through a liquid nitrogen cooled trap to a NRC B-2 oil booster pump backed by a  $\frac{1}{3}$  hp (248 W) rotary mechanical pump (Welch DuoSeal 1400).

The tube (not shown in Fig.1) leading to the desorption cell,  $V_1$ , for measurement of the pressure was 2.7 mm id and 2.5 cm long between  $V_1$  and  $V_2$  and 5.8 mm id and 81.3 cm long between  $V_2$  and the top of the cryostat. The pressure in the desorption cell was measured by various gauges located at room temperature, including, for the final pressures,  $p_f$  reported below, helium calibrated Veeco thermocouple gauges, types DV3M (0–1 000  $\mu\text{m}$ ) and DV5M (1–100  $\mu\text{m}$ ).

After each cryostat was cooled to 4.2 K, an experimental desorption run proceeded first by adjusting  $V_2$  to a desired initial temperature,  $T_i$ , with exchange gas within it so that  $V_1$  attained the same temperature. Then dried  $\text{He}^4$  gas of purity 99.995% after passing through a charcoal

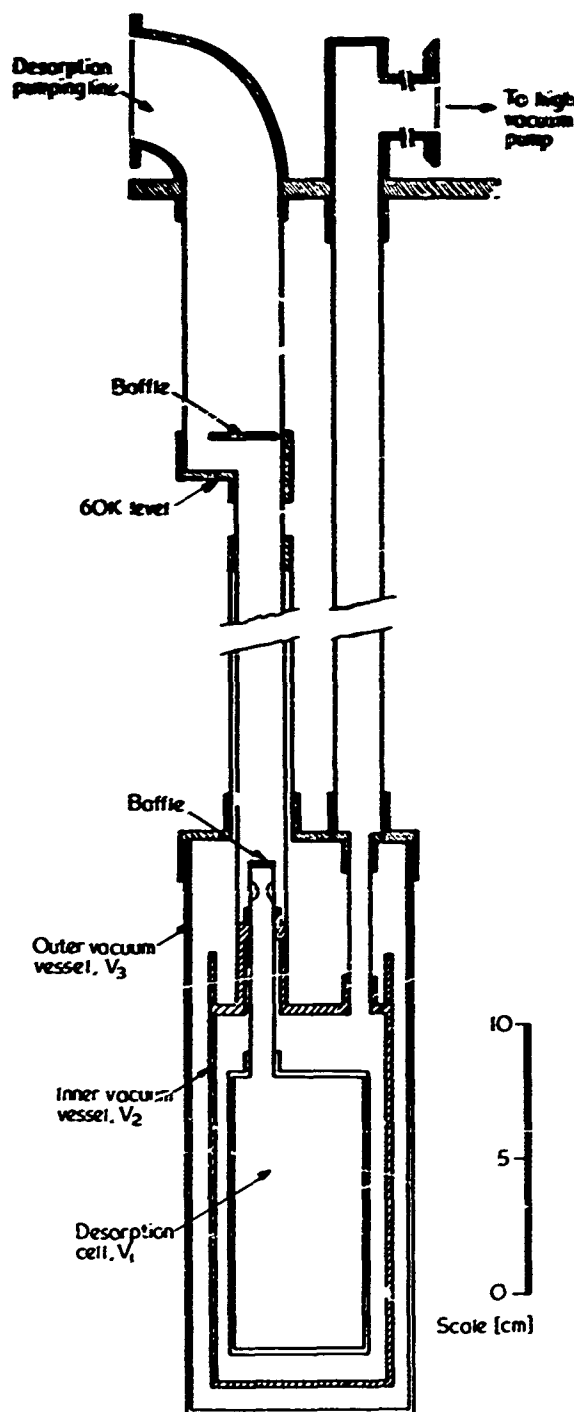


Fig. 1 Scale drawing of the second desorption cryostat (System B) in section

purifier maintained at 77.4 K, was introduced into  $V_1$  to a predetermined initial pressure,  $p_i$ . When equilibrium was attained,  $V_1$  was thermally isolated. This was achieved by high-vacuum pumping of  $V_2$ . The desorption was initiated immediately thereafter, after  $p_i$  and  $T_i$  were recorded.

Desorptions were carried out using the 1400 Welch mechanical pump for pumping on the desorption cells and, in the case of System B, using in addition the NRC B-2 Booster Pump. The final pressures,  $p_f$

obtained in the desorption cell with zero power loading were: (1) without the Booster Pump at not 50 to 70  $\mu\text{m}$  for pumping with the mechanical pump alone and (2) about 10 to 13  $\mu\text{m}$  for pumping with the Booster pump. These pressure values are corrected ones, corrections having been made in the case of System B for thermomolecular pressure effects<sup>18</sup> and in the case of System A for the pressure drop due to the gas flow up the tube between the desorption cell and the gauge, as well as for the thermomolecular pressure effects.

In each desorption run the temperature of the desorption cell and its pressure were observed throughout the duration of the run. Moreover measured heating powers were applied in varying amounts, when desired, to the desorption cell and the resulting temperature and pressure changes observed.

### 3. The experimental results

The initial data of interest are the minimum final temperatures,  $T_{f,\min}$  and their associated pressures,  $p_f$ , attained by desorption from various initial temperatures,  $T_i$ , and pressures,  $p_i$ . The observed results, obtained using both cryostats (System A and System B) are presented in Tables 2 and 3, which also include sample data on the

Table 2. Desorption experiments data taken without use of booster pump (final pressure 50 to 70  $\mu\text{m}$ )

$T_i$ , K	$p_i$ , atm	$T_{f,\min}$ , K	$r = T_i/T_{f,\min}$	$\tau_{\min}$
6.0	0.95	1.83	3.28	15
8.0*	0.25	4.80	1.67	10
8.0	0.48	3.70	2.16	35
8.0*	0.50	3.64	2.20	10
8.0	0.50	3.72	2.15	35
8.0	0.50	3.75	2.13	40
8.0	0.83	3.31	2.42	20
8.0*	1.00	3.07	2.61	10
8.0	1.06	3.25	2.46	30
10.0*	0.25	7.04	1.42	—
10.6*	0.50	6.10	1.64	—
10.0	1.00	4.85	2.06	—
12.0*	0.25	9.45	1.27	—
12.0*	0.50	8.51	1.41	—
12.0*	1.00	7.27	1.65	—

\* The data marked with an asterisk were taken using System A.

Table 3. Desorption experiments data taken with use of booster pump (final pressure 10 to 13  $\mu\text{m}$  (System B))

$T_i$ , K	$p_i$ , atm	$T_{f,\min}$ , K	$r = T_i/T_{f,\min}$
8.0	0.50	3.20	2.50
8.0	0.50	3.10	2.58
8.0	1.06	2.72	2.94

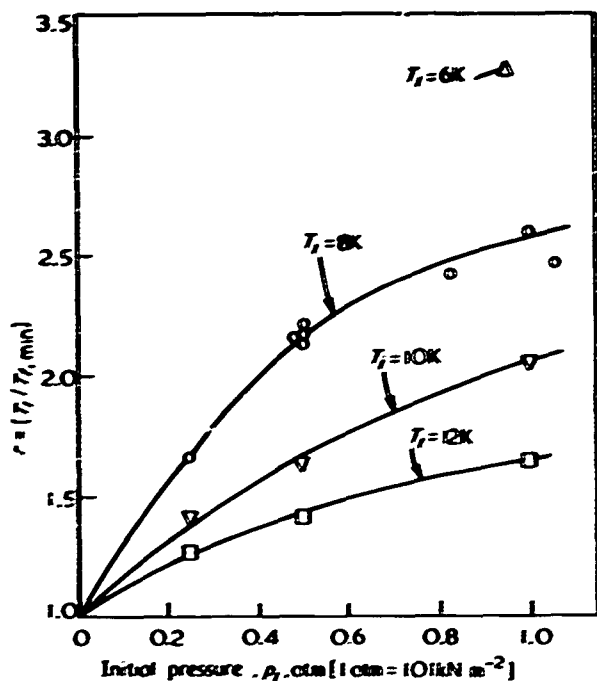


Fig. 2 Plot of the observed  $r$  values ( $r = T_i/T_{f,min}$ ) versus initial pressure,  $p_i$ , for several values of the initial temperature,  $T_i$ . The data were taken using the mechanical pump only

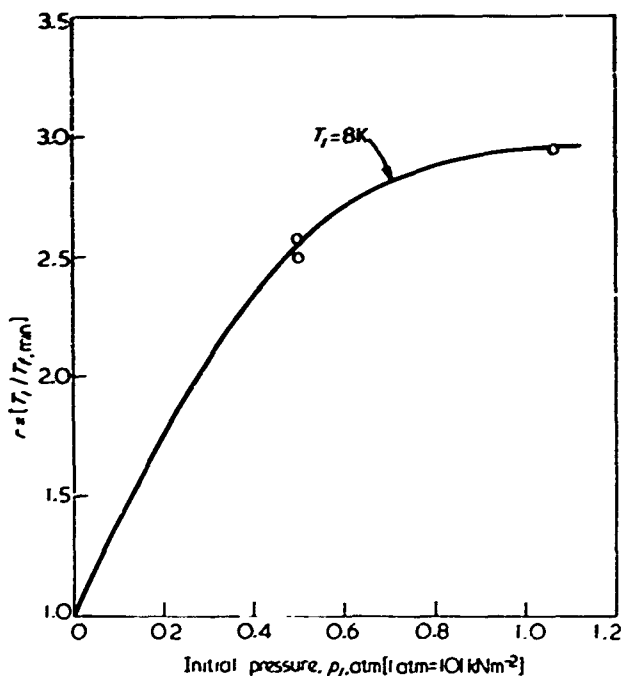


Fig. 3 Plot of the observed  $r$  value ( $r = T_i/T_{f,min}$ ) versus initial pressure,  $p_i$ , for initial temperature,  $T_i$ , of 8.0 K. The data were taken using the Booster and the mechanical pump

time,  $\tau_{min}$ , taken to reach  $T_{f,min}$  from the initial conditions and evaluation of the ratio  $r$ , where  $r = T_i/T_{f,min}$ . Table 2 gives the results for desorption using the mechanical pump (Welsh model 1400) only for both System A and System B, whereas Table 2 presents the results obtained for desorption using the

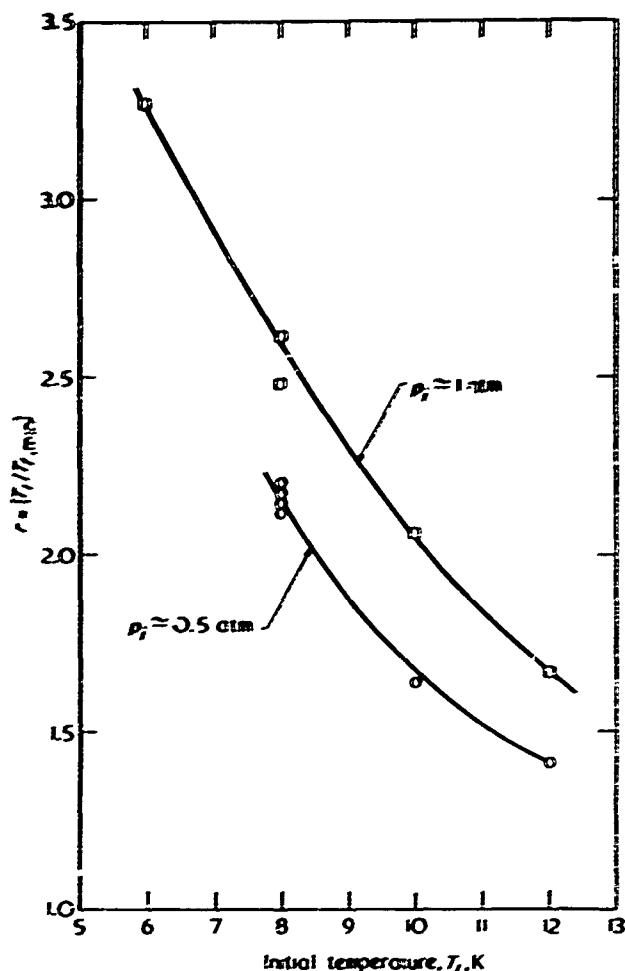


Fig. 4 Plot of the observed  $r$  values ( $r = T_i/T_{f,min}$ ) versus initial temperature,  $T_i$ , for two initial pressures  $p_i = 0.5$  atm approx and  $p_i = 1$  atm approx. The data were taken using the mechanical pump only

Booster Pump as well as the mechanical pump on System B only.

Fig. 2 shows a plot of the observed  $r$  values as a function of initial pressure,  $p_i$ , for initial temperatures,  $T_i$ , of 6.0 K, 8.0 K, 10.0 K, and 12.0 K for desorption to pressure ( $p_f$ ) of 50 to 70  $\mu$ m (mechanical pumping only). Fig. 3 shows a plot of the observed  $r$  values as a function of initial pressure,  $p_i$ , for initial temperature  $T_i = 8.0$  K for desorption to 10 to 13  $\mu$ m (Oil diffusion Booster Pump). It will be seen that the ratio,  $r$ , for a given pumping arrangement increases monotonically with increasing  $p_i$  and, at constant  $p_i$ , increases with increasing  $T_i$ . Also the increase in the ratio,  $r$ , for desorption using the Booster pump with System B is clearly shown for the  $T_i = 8.0$  K and  $p_i = 0.5$  atm (1 atm = 101 kN m<sup>-2</sup>). use of the Booster Pump decreases the value of  $T_{f,min}$  by about 15% below the value obtained with the mechanical pump alone.

Fig. 4 presents the desorption data, plotting the ratio,  $r$ , versus the initial temperature,  $T_i$ , for different initial pressures,  $p_i$ , of about 0.5 and 1.0 atm and for desorption to  $p_f$  values between 50 and 70  $\mu$ m. It is

evident that the  $r$  values increase markedly as the initial temperature is decreased.

The temperature-time history of a typical desorption run is shown in Fig. 5 which is for a run starting with  $T_i = 8.0$  K and  $p_i = 0.5$  atm. In this figure it will be seen that the desorption was first made using the mechanical pump alone, with which the final temperature was reduced to 3.75 K in about 40 minutes, and thereafter the temperature remained essentially constant until minute 98. At this time the Booster Pump was activated and further desorption cooling occurred and in about 20 minutes the temperature fell to a steady value of 3.20 K. It remained at 3.20 K for approximately 20 minutes with a very small warm-up rate, after which time 5.0 mW of heat was supplied to the sample by means of the electrical heater. This heating was maintained until minute 250 and the desorption cell settled down to a reasonably steady rate of warming during this period. At minute 250 the heating was increased to 12.8 mW and was maintained at this value until minute 516. The rate of warming during this period is shown on the graph of Fig. 5. At minute 516 the heating was cut off and at the same time the Booster Pump was deactivated, so that the pumping from this time on was by the mechanical pump alone. By minute 1304, when the run was terminated, the temperature of the adsorption cell had fallen to 4.35 K.

Many desorption runs similar to that shown in Fig. 5 were made and from them the heating rates,  $dT/dt$ , for various input heating powers  $P$ , and at various values of the average temperature and pressure were determined. Typical data obtained in this way, using System B, are shown in Fig. 6, which plots two curves of the steady warming rate ( $dT/dt$ ) versus the heating power,  $P$ , for warmings at about  $3.5$  K  $\pm 0.1$  K and at about  $5.5$  K  $\pm 0.3$  K. The numbers in parenthesis to the right of each point in Fig. 6 give the average pressure in microns, which varies here from 19 to 36 microns. It is evident that these values of ( $dT/dt$ ) increase approximately linearly with  $P$  and grow larger as the average temperature is reduced at constant  $P$ . It is further evident that the zero power rate of temperature rise is quite small, ( $dT/dt$ )  $\leq 5$  mK s<sup>-1</sup>. By extrapolation of the curves backwards, one estimates that the heat leak to the adsorption cell (System B) in the absence of heater power ( $P = 0$ ) lies between 0.2 and 0.5 mW.

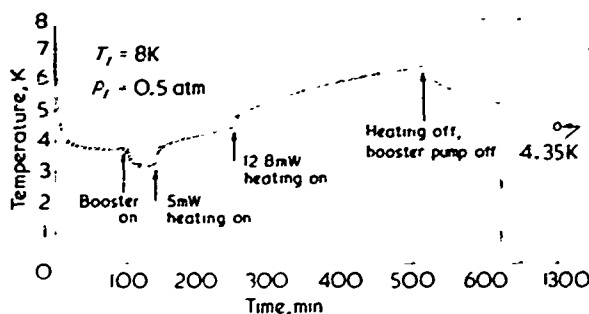


Fig. 5 Plot of temperature versus time for a typical run with system B with  $T_i = 8.0$  K and  $p_i = 0.5$  atm. For detailed commentary see text.

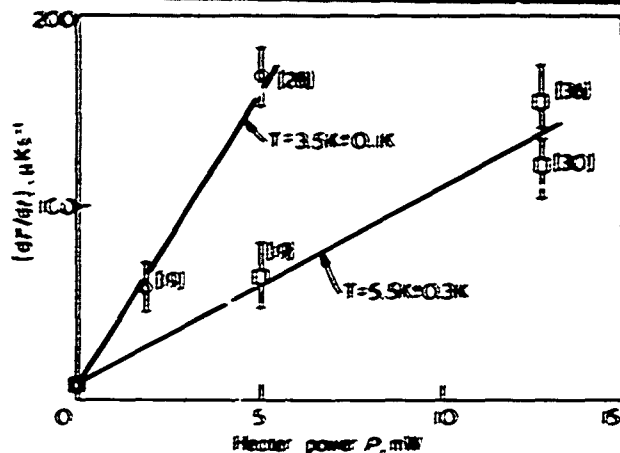


Fig. 6 Plot of observed warm-up rates, ( $dT/dt$ ) in micro-Kelvin per sec. versus heater power,  $P$ , in milliwatts for the System B. The two curves are for average temperatures  $3.5$  K  $\pm 0.1$  K and  $5.5$  K  $\pm 0.3$  K. The numbers in parentheses to the right of each point give the average pressure in the desorption cell in microns.

#### 4. Discussion

It is of interest to consider in connexion with our results the variables which affect the low temperature reached, and in particular  $T_{f, \min}$ , in the desorption process. For a given adsorbent material and working gas, the major variables are:

1. The initial temperature,  $T_i$
2. The initial pressure,  $P_i$
3. The heat capacity of the desorption cell and its addenda
4. The residual heat leak into the desorption cell and, if applied, the power dissipated in the cell
5. The throughput and pressure capability of the pump
6. The flow resistance of the pumping line
7. The flow resistance within the pores of the adsorbent material.

Considering first item (3), the heat capacity of the desorption cell and its addenda, we note that for System A the mass of copper in the desorption cell was 24.2 g and that for System B 286 g. If we consider, as an example, a cooling from 8.0 K to 4.0 K, the enthalpy difference,  $\Delta H$ , for the copper between these two temperatures is about 0.024 J for System A and 0.28 J for System B. This is to be compared with the heat of desorption in each system. Taking, as previously reported by us,<sup>10</sup> the heat of desorption at 2-layer coverage to be about 500 J mole<sup>-1</sup>, the surface area of the synthetic zeolite 13X to be 527 m<sup>2</sup> g<sup>-1</sup> and a 'layer' to be about 0.3 cm<sup>3</sup> (STP) m<sup>-2</sup>, then the total heat of desorption per layer (at about 2 layers coverage) is about 12.5 J for System A and 460 J for System B. It appears therefore that in the desorption process, the cooling of the copper part of the desorption cell, imposes a very small load on the coolant process at these low temperatures. However, as is discussed later, the total heat capacity of the

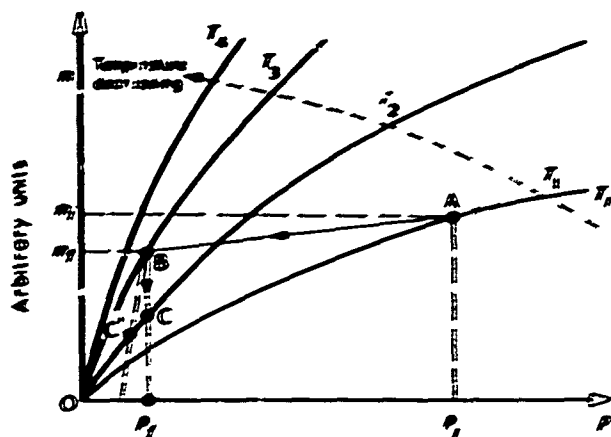


Fig.7 Sketch of a typical family of adsorption isotherms plotting the mass adsorbed,  $m$ , versus pressure  $p$ . Four typical isotherms are shown, where  $T_1 > T_2 > T_3 > T_4$ . The path A-B-C represents a desorption run. For detailed commentary, see text.

desorption cell of System A, including its addenda and the zeolite, may be of some significance relative to the cooling power of the desorption process, due to the relatively small amount of zeolite employed. At much higher temperatures, for example liquid nitrogen temperatures, this favourable high 'loading' of the desorption cell is no longer valid, as we have found in separate experiments.<sup>19</sup> For initial temperatures therefore below about 12 K, it is possible, at least for the larger cryostat (System B) to neglect in first approximation the effect of item (3), the heat capacity of the desorption cell and its addenda and contents, on the cooling process.

One may therefore consider the cooling process, for sufficiently low initial temperatures as described above, to be as indicated in Fig.7 which sketches a family of typical equilibrium adsorption isotherms of the mass adsorbed versus vapour pressure. Note that  $T_1 > T_2 > T_3 > T_4$ . If the initial mass adsorbed is  $m_i$  and the initial pressure,  $p_i$ , represented by the point A, then a desorption would be represented by the path A-B, where at B the mass adsorbed is  $m_f$  ( $m_f < m_i$ ) and the pressure  $p_f$  ( $p_f < p_i$ ). There is also a contribution to the cooling process due to isentropic expansion of the gas from the void volume of the adsorption cell (Simon expansion<sup>20</sup>). This results in further reduction of the difference between  $m_f$  and  $m_i$ .

For adequately low values of  $T_i$ , as discussed above, the difference between  $m_f$  and  $m_i$  would be small, as sketched in Fig.7. The final temperature reached (in Fig.7, this is  $T_3$ ) therefore is determined by  $p_f$ . Each adsorbent will have its own characteristic family of isotherms similar to that sketched in Fig.7 and hence for a given  $p_f$  the value of  $T_f$  will be characteristic of the material used. For synthetic zeolite 13X the isotherms between 4.2 K and 20.0 K have been published by us elsewhere.<sup>10,11</sup>

A comparison of the data reported here with estimates of desorption collings calculated from our previously measured isotherms shows that for  $T_i = 6.0$  K and 8.0 K there is good self-consistency. (Quantitative comparisons however are not possible because the isotherm data does not go below

4.2 K). In comparing in the same way the collings obtained with  $T_i = 10.0$  K and 12.0 K we find that the desorption experiments did not reach to temperatures as low as one would expect from the isotherms by putting  $m_f \approx m_i$ . This may be interpreted as an indication that for the small volume cryostat (System A) the  $m_f$  values were appreciably less than the  $m_i$  values, due presumably to a non-negligible relative heat content of the desorption cell and its addenda at these higher values of  $T_i$ .

Now  $p_f$  in practical situations is determined generally by dynamical considerations that are largely independent of the adsorbent material but that are determined by the apparatus used. In practice there is always some heat leak into the adsorbent material and there may be some refrigerative load applied. To offset this heat input power,  $p_i$ , there must be a continuous desorption, in amount  $m \leq \dot{m}$ , given by  $P = Q\dot{m}$ , where  $Q$  is the heat of desorption at the point ( $m_f, p_f$ ). In any given apparatus, the gas flow  $m$  from adsorbent to pump will in general determine  $p_f$  the variables (5), (6), and (7) being those which are appropriate in this determination.

For the apparatus used in our experiments, both for System A and System B, we know in detail the values of (4), (5), and (6). The residual heat leak into desorption cell of System A was about 25  $\mu$ W, whereas as that into the cell of System B was (as stated earlier) from 200  $\mu$ W to 500  $\mu$ W. Moreover, as reported in section 3, many input powers were applied to the desorption cell of System B in amounts up to 12.8 mW. The approximate values of the heat of adsorption (desorption) are known for He<sup>4</sup> on synthetic zeolite from our previous work.<sup>10,11</sup>

Item (5), the characteristics of the pump are known and item (6), the flow resistance of the pumping tubes was estimated in a manner similar to that previously employed by one of us (JGD).<sup>21</sup> In the situation here, account was taken of the change from Poiseuille flow to Knudsen flow as one went up the pumping tube towards room temperature. The evaluations of items (4), (5), and (6) at our disposal in this way lead to the following conclusions:

(a) The primary limitation on  $p_f$  and hence on  $T_f$  for System A and System B, when used with the Booster Pump, was the flow resistance of the pumping tubes. Larger tubes with lower resistance would result in lower  $T_f$  until limitations due to items (5) or (7) would be encountered.

(b) The primary limitation on  $p_f$  and hence on  $T_f$  for System B using the mechanical pump alone was the pump itself, that is, item (5).

(c) No evidence was apparent for any limitation on  $p_f$  due to pressure drops within the pores of the adsorbent. This may appear at first somewhat surprising in view of the finding in earlier work<sup>21</sup> that this process was a limiting factor in adsorption pumping using coconut charcoal grains as adsorbent. It is not in fact contradictory however when one considers the much higher pressures that are obtained in the present experiments. It should be noted however that this factor may become of significant influence if desorptions to much lower temperature than those reported here were to be carried out.



Some remarks may be made concerning the observed warm-up rates when significant powers were applied to the desorption cell. For a given power,  $P$ , the gas flow  $\dot{m}$  will remain approximately constant provided there is not too much depletion of the mass adsorbed (A discussion of the effect of depletion is given immediately below). For a steady pumping regime therefore, for a given power  $P$  there will be a dynamically equilibrium value of  $p_f$ . In first approximation therefore, the state of the system will follow a constant pressure line, as indicated by the line B-C in Fig. 7. This line is one of warming and the rate of warming is determined by the value of  $(\partial m/\partial T)_p$  in the region B-C, i.e. we have:

$$P = -Q\dot{m} = -Q \left( \frac{\partial m}{\partial T} \right)_p \left( \frac{dT}{dt} \right) \quad (1)$$

It should be observed that  $(\partial m/\partial T)_p$  is a function of  $T$  and  $p$ . To assess its variation with  $T$  and  $p$  we have used our previous adsorption data<sup>10,11</sup> and obtained  $(\partial m/\partial T)_p$  graphically. Fig. 8 gives the data for four pressures, namely 10, 50, 100, and 200  $\mu$ m. The values of  $(\partial m/\partial T)_p$  which are all negative, are expressed in  $\text{cm}^3$  (STP) of  $\text{He}^4$  per  $\text{cm}^2$  of adsorbing zeolite 13X per degree K. It will be observed that between 3.5 K and 7.5 K,  $(\partial m/\partial T)_p$  is a strong function of  $T$ , approximately doubling in absolute value in this temperature range. It is, however, far less dependent on  $p$ . For example at 3.5 K it is almost independent of  $p$  in the pressure range 10 to 200  $\mu$ m, whereas at 5.5 K it varies within a range of  $\pm 5\%$  for pressure changes between 10 and 50  $\mu$ m.

For the data of Fig. 6 therefore, where the pressure range was from 19 to 36  $\mu$ m, one may take the first approximation  $(\partial m/\partial T)_p$  to be constant at any selected average temperature. In this case equation 1 would predict an approximately linear relation between  $(dT/dt)$  and  $P$  for the conditions obtaining in these experiments, and this is supported by the experimental data presented in Fig. 6.

Our experimental data moreover show that the warm-up rate  $(dT/dt)$  at a given power level increases with decreasing average temperature. For example at  $P = 5.0$  mW, the ratio of  $(dT/dt)$  at  $T \approx 3.5$  K to that at  $T \approx 5.5$  K is approximately 2.7:1. From Fig. 8 one notes that the ratio of the value of  $(\partial m/\partial T)_p$  at 5.5 K to its value at 3.5 K for pressures between 19 and 28  $\mu$ m is approximately 2.5:1. Since the value of  $Q$  is approximately independent of  $T$ , the agreement between these two ratios (at least within the error of our knowledge of the values of  $(\partial m/\partial T)_p$  apparent here) provides good confirmation of the general validity of equation 1.

Now a comment regarding lengthy periods of refrigeration with the desorption system, as for example was carried out from minute 250 to minute 516 in the desorption run using System B which is shown in Fig. 5. It will be seen in the figure that  $(dT/dt)$  diminished gradually over this period. This can be attributed to significant depletion of the mass adsorbed. In fact, for this run the mass adsorbed decreased from approximately  $0.4 \text{ cm}^3$  (STP)  $\text{m}^{-2}$ . As has been shown earlier<sup>10</sup> by us for  $\text{He}^4$  on 13X, the heat of desorption,  $Q$ , increases

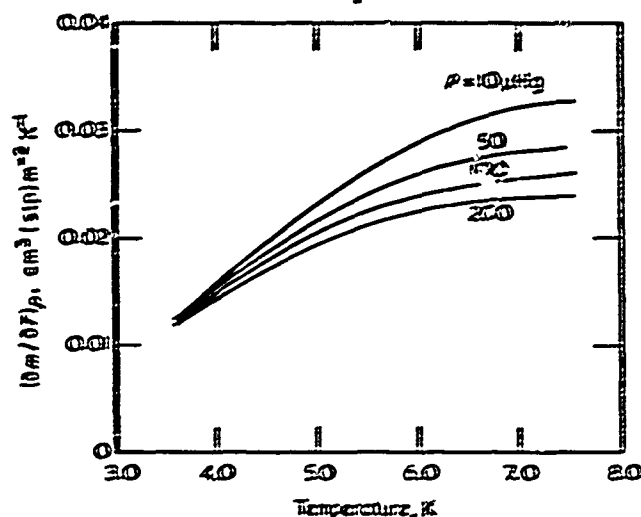


Fig. 8 Plot of  $(\partial m/\partial T)_p$  versus  $T$  for various pressures, calculated from adsorption data for the  $\text{He}^4$  on zeolite 13X reported earlier by Dunt and Flood<sup>10,11</sup>. The numbers on each curve give the isobaric pressures in microns. Note that  $(\partial m/\partial T)_p$  is a negative quantity

Table 4. Warm-up times,  $\Delta t$ , and total energy absorbed,  $\Delta E$ , for a desorption refrigerative system with synthetic zeolite (13X) of mass 1 kg in various temperature ranges for three refrigerative power loadings of 1 mW, 5 mW, and 10 mW, for a well isolated desorption cell (see text)

Power	Temperature		
	From 3 K to 4 K	From 4 K to 5 K	From 5 K to 6 K
1 mW	$\Delta t = 64$ hours $\Delta E = 230$ J	$\Delta t = 130$ hours $\Delta E = 460$ J	$\Delta t = 200$ hours $\Delta E = 730$ J
5 mW	$\Delta t = 12.8$ hours $\Delta E = 230$ J	$\Delta t = 26$ hours $\Delta E = 460$ J	$\Delta t = 40$ hours $\Delta E = 730$ J
10 mW	$\Delta t = 6.4$ hours $\Delta E = 230$ J	$\Delta t = 13$ hours $\Delta E = 460$ J	$\Delta t = 20$ hours $\Delta E = 730$ J

as  $m$  is decreased. This increase in  $Q$ , which would take place gradually will result in a diminution of  $(dT/dt)$  for constant power  $P$ , as is evident from equation 1 and reflected in Fig. 5.

The increase in  $Q$  during these periods of prolonged pumping moreover results in a corresponding decrease in  $\dot{m}$  when  $P$  is constant, in order to preserve  $P = -Q\dot{m}$ . Since  $\dot{m}$  and  $p_f$  are directly related to each other, prolonged pumping also results in a gradual (small) decrease in  $p_f$ . For example in the run illustrated in Fig. 5,  $p_f$  decreased from 38  $\mu$ m at minute 250 to 35  $\mu$ m at minute 500. Such an effect is qualitatively illustrated in the diagram of Fig. 7 by the broken path line B-C'.

Finally it may be of interest to tabulate some derived data for a desorption system similar in general features to our System B, but modified for and normalized to a change of synthetic zeolite 13X of 1 kg, which data are directly computed from the results given in the previous section. Table 4 shows these data for the elapsed time,  $\Delta t$ , and the total energy absorbed,  $\Delta E$ , for a kilogram system for various power inputs (1 mW, 5 mW, and 10 mW) for temperature excursions between (a) 3 K to 4 K, (b) 4 K to 5 K, and (c) 5 K to 6 K. In computing  $\Delta t$  it has been assumed that the zero-power ( $P=0$ ) heat input to the desorption system is negligible. It will be noted, for example, that for a 1 mW refrigerative load a 1 kg system would last 130 hours in the temperature range 4 K to 5 K. The data of Table 4 are conservative, based on a total reduction of coverage of helium from an approximately  $0.4 \text{ cm}^3 \text{ (STP) m}^{-2}$  to about  $0.3 \text{ cm}^3 \text{ (STP) m}^{-2}$  between 3 K and 6 K.

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## References

1. Daint, J. G., and Coors, W. S. Office of Naval Research Report, Contract Nona-263 (70) (1969)
2. Weinstein, A. I., Friedman, A. S., and Coors, W. S. *Advances in Cryogenic Engineering* 9 (1964) 429
3. Simon, F. *Phys Zeit* 21 (1928) 196; *Zeit f ges Techindustrie* 34 (1927) 217 and *Physica* 4 (1937) 379
4. Mendelssohn, K. *Zeit f Phys* 13 (1931) 432
5. Keesom, A. Van and Van Dingenen, W. *Physica* 5 (1938) 529 and *J Phys Radium* 11 (1940) 25
6. Kevins, E. *Chem Soc Japan Bull* 13 (1938) 241
7. Boudry, L., and Reichel, J. *Cryogenics* 2 (1962) 189
8. Daint, J. G. Proc ICECL, Kyoto, Japan (1967) 195
9. Daint, J. G. *Prog Refrig Sci and Tech* 1 (1963) 47
10. Daint, J. G., and Coors, C. Z. *J Low Temp Phys* 3 (1970) 89
11. Daint, J. G., and Coors, C. Z. Proc Fifth Symp Thermophysical Properties (ASME, 1970) 319
12. Daint, R. M. *Emblemur* 23, (1964) 122
13. Back, R. W. *J Chem Ed* 43 (1964) 673
14. Daint, R. H. E., and Minisoff, G. I. *Discovery* (Dec 1964) 32
15. Daint, R. M., Balford, F. W., and Sutherland, J. W. *Trans Faraday Soc* 53, (1957) 1111
16. Mason, F. Union Carbide Corp (private communication)
17. Renner, S. The Adsorption of Gases and Vapors, Vol I. Physical Adsorption (Princeton Univ Press, 1945)
18. Roberts, T. R., and Sydnor, S. G. *Phys Rev* 102, (1956) 306
19. Daint, J. G., and Coors, C. Z. (unpublished)
20. Simon, F. *Phys Zeit* 34 (1933) 252
21. Mott, C. F., Harris-Lowe, R., Davis, W. C., and Daint, J. G. *Rev Sci Instr* 36 (1965) 569